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# EFFECTS OF PRESSURE ON BINARY ALLOYS

# MISCELLANEOUS EFFECTS OF PRESSURE ON MISCELLANEOUS SUBSTANCES

By P. W. Bridgman

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# Effects of Pressure on Binary Alloys

## III

### Five Alloys of Thallium, including Thallium-Bismuth

By P. W. Bridgman

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## Introduction

In this third paper of the series[1] several alloys are described for which the phase diagrams are complicated by the presence of a high pressure transition of one of the components, thallium. In the fourth paper the alloys of bismuth will be described, which have a similar complication, only more elaborate, because bismuth has several pressure transitions instead of the one of thallium. The alloys containing bismuth therefore have a greater wealth of detail than those with thallium, and accordingly the experimental material is more extensive. The alloys of thallium with bismuth, containing both complications, are being described in this paper instead of the following one in order to more evenly distribute the length of the two papers. In this paper new data are given for the pure component, thallium, as well as for the alloys.

## Detailed Presentation of Data

*Thallium.* Various data for the effects of pressure on the pure metal have been obtained in the past,[2] but in order that the results should be on the same material as that from which the alloys were made some of the former measurements have been repeated.

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The material used in the present work was obtaind from MacKay, described as "99.9 plus pure." The measurements now made on this MacKay material were, specific resistance and temperature coefficient of resistance at atmospheric pressure, compression to 40,000 kg/cm$^2$, shearing to 80,000 kg/cm$^2$, and resistance to 100,000 kg/cm$^2$. Among my previous measurements were specific resistance and temperature coefficient of resistance, and resistance to 30,000 and 100,000 kg/cm$^2$. These measurements were made on material given to me by the Harvard Chemical Laboratory, being stock found in the laboratory of Professor T. W. Richards after his death. I was told that this was material which he had used in his atomic weight determinations. The implication, understood by both the Chemical Laboratory and by me, was that this was highly purified material. My suspicions were aroused, however, by the discovery that the temperature coefficient of this was not materially different from that of my MacKay material and very materially lower than the temperature coefficient of the material on which I had made measurements in 1917. This latter had been subjected to a number of chemical transformations for my measurements of the effect of pressure on polymorphic transitions. It was received as pure metal, then successively converted to nitrate, iodide, and sulfate, and finally electrolyzed back to the pure metal. These various transformations would be expected to result in metal of high purity. This is confirmed by the temperature coefficient, which was 0.00517 between 0° C and room temperature, against 0.00436 for the material from T. W. Richards and 0.00434 for the present material from MacKay. Another specimen of thallium was also investigated: this I owe to the courtesy of Professor N. Bloembergen, who obtained it from the Research Laboratories of the Thallium Corporation. The exact analysis was not given, but the impurities were stated to be in the hundredths of a per cent. The temperature coefficient of this was 0.00446 and specific resistance at 0° $16.87 \times 10^{-6}$. The specific resistance of the MacKay material was 16.94 and that of Professor Richards $17.4 \times 10^{-6}$. It seems probable that the three materials are much alike, with the specimen of Professor Bloembergen somewhat the best of the three, but that none of them approached in purity my own electrolytic material of 1917. Unfortunately the specific resistance of this was not determined.

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The various data for MacKay's thallium are given in the tables with the several alloys. The present values for the effect of pressure on resistance differ somewhat from those previously published on presumably the same material. In this connection it is to be remembered that precise reproducibility in resistances under pressure is not to be expected because thallium does not crystallize in the cubic system. Properly, the measurements on thallium should have been made on a single crystal and the variation with orientation determined. I did not, however, prepare any single crystal material. A difficulty encountered in an exploratory attempt was the fact that molten thallium attacks glass on prolonged contact.

*Thallium-Cadmium.* This system, according to Hansen[3], is a simple eutectic between practically pure cadmium and thallium, with at most a very small percentage of dissolved cadmium. Four compositions were investigated: 20, 40, 60, and 80 atomic per cent. The homogeneity of the castings is vouched for by the fact that the observed densities agree with the calculated densities to the second decimal place, and in the two cases investigated there was no significant difference of density between different parts of the same casting. The specimens for the resistance measurements to 30,000 were extruded at 170°. The specific resistance against composition lies on a smooth curve. The values for specific resistance and temperature coefficient give no reason to think that there is appreciable mutual solubility at either end of the series at room temperature.

The observed changes of resistance under pressure, compressions, specific resistances, temperature coefficients of resistance, and densities are given in Table I. In general the plot against composition is a more or less smooth curve joining the points for the pure components, with no intermediate episodes, as would be expected from the eutectic composition.

The transition of pure thallium occurs between 40,000 and 45,000 kg/cm$^2$, too high to appear on the compressions, which were measured to only 40,000. The transition does appear in the resistance data, however. The break in resistance which marks the transition occurs at progressively higher pressures with increasing cadmium content, reaching 60,000 kg/cm$^2$ at the 80 – 20 composition. The explanation of this may well be merely a super-

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# TABLE I

## Thallium – Cadmium System

| | 100 Tl | 80 Tl 20 Cd | 60 Tl 40 Cd | 40 Tl 60 Cd | 20 Tl 80 Cd | 100 Cd |
|---|---|---|---|---|---|---|
| Density | 11.86 | 11.35 | 10.78 | 10.13 | 9.41 | 8.62 |
| $\rho_{00} \times 10^6$ | 16.9 | 15.0 | 11.9 | 9.4 | 8.0 | 6.4 |
| Temperature Coefficient | .00434 | .00421 | .00409 | .00408 | .00407 | .00401 |
| Pressure kg/cm² | | | Rp/Ro | | | |
| 0 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 |
| 5,000 | .936 | .942 | .946 | .952 | .955 | .961 |
| 10,000 | .882 | .892 | .901 | .911 | .917 | .927 |
| 15,000 | .832 | .848 | .860 | .875 | .884 | .897 |
| 20,000 | .795 | .811 | .826 | .844 | .855 | .872 |
| 25,000 | .760 | .777 | .795 | .817 | .830 | .849 |
| 30,000 | .727 | .748 | .768 | .792 | .807 | .828 |
| 40,000 | .665<br>.487 | .699 | .719 | .747 | .767 | .792 |
| 50,000 | .436 | .657<br>.549 | .679<br>.588 | .710<br>.646 | .733 | .762 |
| 60,000 | .391 | .517 | .553 | .613 | .702<br>.680 | .736 |
| 70,000 | .352 | .489 | .524 | .582 | .654 | .713 |
| 80,000 | .319 | .463 | .498 | .555 | .632 | .693 |
| 90,000 | .290 | .438 | .474 | .532 | .612 | .675 |
| 100,000 | .265 | .416 | .453 | .511 | .601 | .658 |
| | | | $-\Delta V/Vo$ | | | |
| 5,000 | .0137 | .0132 | .0123 | .0125 | .0113 | .0108 |
| 10,000 | .0263 | .0253 | .0237 | .0235 | .0214 | .0201 |
| 15,000 | .0379 | .0364 | .0343 | .0336 | .0311 | .0290 |
| 20,000 | .0484 | .0469 | .0443 | .0434 | .0401 | .0372 |
| 25,000 | .0587 | .0566 | .0534 | .0521 | .0487 | .0449 |
| 30,000 | .0684 | .0655 | .0622 | .0606 | .0565 | .0518 |
| 35,000 | .0775 | .0740 | .0704 | .0682 | .0640 | .0584 |
| 40,000 | .0859 | .0814 | .0780 | .0759 | .0711 | .0640 |

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cooling effect, the amount of which increases with the dilution of the thallium; this is perhaps not unnatural. The ratio of the resistances at the transition, before to after, rises continuously with composition, and except for the value for Cd 20 – Tl 80, linearly within a small error. The exceptional point would not appear to be off the line by a significant amount.

The shearing curves are not particularly sensitive to the transition of thallium. The curve for pure thallium has a cusp at 20,000 kg/cm$^2$ at which the tangent of the shearing curve breaks upward (this is not the known transition) followed by another cusp at 45,000 (the previously known transition), at which the tangent breaks downward, but by a small amount. From here the shearing strength rises to 1,140 kg/cm$^2$ at a pressure of 80,000 kg/cm$^2$. The two cusps, in approximately the same locations, become somewhat accentuated in the alloys, the shearing strengths of which are in general greater than for pure thallium. The shearing strengths at 80,000 of the 80, 60, 40, and 20 thallium compositions are respectively: 2,600, 1,820, 1,720 and 1,680 kg/cm$^2$. The shearing curve for pure cadmium, on the other hand, rises approximately linearly over the entire range, but with a slight upward break in the tangent at 30,000, to 2,480 kg/cm$^2$ at a pressure of 80,000.

Neither the resistance nor the shearing measurements indicate any radical difference above 45,000 between the cadmium alloys of the high pressure modification of thallium as compared with the alloys of the low pressure modification.

*Thallium-Indium.* According to Hansen[4] the system comprises, at room temperature, a solution of thallium in indium up to about 40 atomic per cent thallium, and a solution of indium in thallium between 60 and 100 per cent thallium, with a mixture of the two limiting solutions between 40 and 60 per cent. The two solubility limits, 40 and 60 per cent, are exceedingly tentative, and in fact no equilibrium points were actually determined below 150°. In any event, the system would appear to be an example of one with unusually wide solubility limits.

In this investigation 15 compositions were measured: 0.2, 1, 2, 5, 10, 20, 40, 50, 60, 70, 77, 83.53, 92, 98, and 99 atomic per cent thallium. Only resistance measurements were made on the 0.2, 1, 2, 98, and 99 per cent compositions, and of these only the first

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was carried to 100,000, the pressure range of the four others being 30,000. The resistance specimens for the measurements at atmospheric pressure and to 30,000 were wires formed by cold extrusion. The specific resistances and the temperature coefficients at atmospheric pressure are shown against composition in Figure 1. At either end of the range the specific resistance rises smoothly, within experimental error, from that of the pure com-

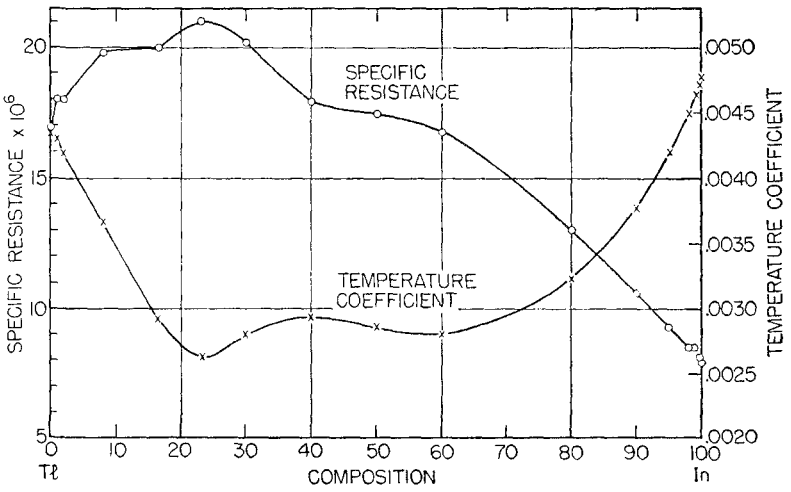


Figure 1. Specific resistance and temperature coefficient of resistance at atmospheric pressure of the thallium – indium system as a function of composition in atomic per cent.

ponents, and the temperature coefficient drops smoothly, as is to be expected of solutions. The intermediate range, between 60 and 20 per cent indium, is not smooth, however, but there is one reversal of trend at 40 per cent shown by both curves. Figure 1 is consistent with Hansen's diagnosis of wide solubility in the two pure components, but the state of affairs at intermediate compositions is probably more complicated than the simple mechanical mixture of limiting solutions suggested by Hansen.

Since the effect of pressure on the phase transitions is in certain respects opposite in the present thallium – indium system from that in the thallium – cadmium system, it will

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pay to briefly review the characteristics of the transitions of thallium. Thallium has a transition between 40,000 and 45,000 kg/cm$^2$ at room temperature at which there is a large drop of resistance. It also has a transition at atmospheric pressure at 230° to a modification with smaller volume. That is, the transition at 230° is of the ice type, temperature falling with rising pressure. This transition has been followed to a triple point at about 150° with the 40,000 room temperature modification[5]. In Hansen's diagram of the thallium – indium system the transition at 230° is shown. The temperature of this transition drops rapidly with increasing indium content. Hansen's diagram would indicate that this transition fades out above 100°, and that even above this the boundaries of the domains of the two phases are somewhat nebulous, being shown by dotted lines.

In the present work four of the compositions richest in thallium, 70, 77, 83.5, and 92 per cent Tl, all in the range of solution of indium in thallium, show a high pressure phase change in the measurements of both resistance and compression. These measurements incidentally place the limits of the homogeneous phase at room temperature at the thallium rich end of the series in the neighborhood of 70 per cent thallium. The phase change indicated by the resistance takes place with considerable hysteresis. The mean pressure of the transition *decreases* with increasing indium content. This is the exact opposite of the behavior in the thallium – cadmium system, where the pressure of the transition *increases* with increasing cadmium content. The magnitude of the discontinuity of resistance increases with decreasing indium content in the present system. A very rough extrapolation of the mean pressures of transition gives a transition pressure for pure thallium of 35,000 kg/cm$^2$. This is close enough to 40,000 to identify the transition as being to the high pressure room temperature modification of thallium (thallium III), as distinguished from the high temperature atmospheric pressure modification (thallium I). The two most dilute solutions, containing 2 and 1 per cent indium, did not show a discontinuity of resistance up to 30,000 kg/cm$^2$. Presumably the discontinuity occurs at a somewhat higher pressure.

The volume discontinuities indicate the same thing as the discontinuities of resistance; in particular the pressure of the discon-

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# TABLE II

## Thallium — Indium System

| | 100 Tl | 99 Tl 1 In | 98 Tl 2 In | 92 Tl 8 In | 83.53 Tl 16.47 In | 77 Tl 23 In | 70 Tl 30 In | 60 Tl 40 In |
|---|---|---|---|---|---|---|---|---|
| Density | 11.86 | 11.82 | 11.77 | 11.52 | 11.14 | 10.78 | 10.55 | 10.10 |
| $\rho_{00} \times 10^6$ | 16.9 | 18.0 | 18.0 | 19.8 | 20.0 | 21.0 | 20.2 | 17.9 |
| Temperature Coefficient | .00434 | .00430 | .00418 | .00365 | .00291 | .00262 | .00280 | .00293 |
| Pressure kg/cm² | | | | | $R_p/R_0$ | | | |
| 0 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 |
| 5,000 | .936 | .938 | .940 | .945 | .949 | .952 | .942 .841 | .943 |
| 10,000 | .882 | .885 | .888 | .896 | .908 | .756[c] | .895 .797 | .894 |
| 15,000 | .832 | .839 | .843 | .855 | .871 .720 | .717 | .758 | .858 |
| 20,000 | .795 | .799 | .804 | .819 | .838 .698 | .684 | .725 | .824 |
| 25,000 | .760 | .765 | .769 | .619[a] | .807 .664 | .654 | .698 | .796 |
| 30,000 | .727 | .733 | .730 | .587 | .635 | .630 | .674 | .771 |
| 40,000 | .665 / .487 | | | .549 | .590 | .592 | .637 | .732 |
| 50,000 | .436 | | | .515 | .555 | .562 | .607 | .704 |
| 60,000 | .391 | | | .485 | .527 | .537 | .584 | .681 |
| 70,000 | .352 | | | .461 | .504 | .517 | .566 | .663 |
| 80,000 | .319 | | | .440 | .487 | .500 | .553 | .648 |
| 90,000 | .290 | | | .422 | .471 | .486 | .540 | .635 |
| 100,000 | .265 | | | .405 | .459 | .473 | .528 | .624 |
| | | | | | $-\Delta V/V_0$ | | | |
| 5,000 | .0137 | | | .0129 | .0138 | .0141 | .0130 .0175 | .0133 |
| 10,000 | .0263 | | | .0252 | .0260 .0313 | .0268 | .0253 .0290 | .0254 |
| 15,000 | .0379 | | | .0364 | .0377 .0428 | .0434[d] | .0404 | .0365 |
| 20,000 | .0484 | | | .0468 | .0485 .0532 | .0539 | .0508 | .0468 |
| 25,000 | .0587 | | | .0634[b] | .0588 .0628 | .0640 | .0606 | .0564 |
| 30,000 | .0684 | | | .0725 | .0728 | .0733 | .0696 | .0654 |
| 35,000 | .0775 | | | .0817 | .0823 | .0819 | .0781 | .0738 |
| 40,000 | .0859 | | | .0907 | .0900 | .0902 | .0857 | .0814 |

(a) Transition at 23,750. Resistances .795 and .626.
(b) Transition at 24,270. Volumes .0558 and .0621.
(c) Transition at 8,400. Resistances .923 and .770.
(d) Transition at 11,700. Volumes .0311 and .0368.

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## TABLE II — *Continued*

### Thallium — Indium System

| | 50 Tl 50 In | 40 Tl 60 In | 20 Tl 80 In | 10 Tl 90 In | 5 Tl 95 In | 2 Tl 98 In | 1 Tl 99 In | 0.2 Tl 99.8 In | 100 In |
|---|---|---|---|---|---|---|---|---|---|
| Density | 9.67 | 9.23 | 8.28 | 7.78 | 7.54 | 7.39 | 7.34 | 7.30 | 7.28 |
| $\rho_{00} \times 10^6$ | 17.4 | 16.7 | 13.0 | 10.6 | 9.3 | 8.5 | 8.5 | 8.1 | 7.9 |
| Temperature Coefficient | .00285 | .00280 | .00323 | .00378 | .00420 | .00449 | .00463 | .00471 | .00478 |
| Pressure kg/cm² | | | | | $R_P/R_0$ | | | | |
| 0 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 |
| 5,000 | .948 | .951 | .946 | .942 | .938 | .940 | .936 | .934 | .933 |
| 10,000 | .904 | .909 | .900 | .893 | .886 | .887 | .880 | .876 | .877 |
| 15,000 | .867 | .874 | .860 | .850 | .840 | .839 | .831 | .829 | .829 |
| 20,000 | .837 | .845 | .826 | .814 | .802 | .799 | .790 | .787 | .786 |
| 25,000 | .810 | .818 | .796 | .781 | .768 | .761 | .753 | .750 | .749 |
| 30,000 | .786 | .796 | .771 | .752 | .737 | .729 | .721 | .718 | .716 |
| 40,000 | .748 | .760 | .731 | .705 | .688 | | | .666 | .666 |
| 50,000 | .719 | .733 | .700 | .667 | .649 | | | .625 | .623 |
| 60,000 | .697 | .711 | .675 | .630 | .615 | | | .589 | .585 |
| 70,000 | .679 | .693 | .654 | .608 | .588 | | | .561 | .554 |
| 80,000 | .664 | .678 | .636 | .586 | .566 | | | .535 | .526 |
| 90,000 | .651 | .663 | .621 | .565 | .545 | | | .513 | .489 |
| 100,000 | .642 | .650 | .608 | .546 | .525 | | | .493 | .473 |
| | | | | | $-\Delta V/V_0$ | | | | |
| 5,000 | .0126 | .0127 | .0132 | .0120 | .0126 | | | | .0127 |
| 10,000 | .0243 | .0244 | .0250 | .0230 | .0237 | | | | .0238 |
| 15,000 | .0354 | .0354 | .0353 | .0335 | .0344 | | | | .0341 |
| 20,000 | .0460 | .0456 | .0457 | .0435 | .0446 | | | | .0439 |
| 25,000 | .0556 | .0549 | .0552 | .0530 | .0542 | | | | .0532 |
| 30,000 | .0646 | .0639 | .0641 | .0619 | .0630 | | | | .0621 |
| 35,000 | .0733 | .0723 | .0725 | .0699 | .0711 | | | | .0708 |
| 40,000 | .0810 | .0802 | .0802 | .0775 | .0790 | | | | .0788 |

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tinuity decreases with increasing indium content. The somewhat irregular values of volume discontinuity extrapolate within experimental error to the value previously found for pure thallium, namely $\Delta V/V_0 = 0.0062$. At 70 per cent thallium $\Delta V/V_0$ is roughly two thirds of its value at 100 per cent.

The corners of the transition curves, for both compression and resistance, are rounded for both directions of the transition, indicating that indium is soluble in both phases, but to different extents. This, and diffusion phenomena, would account for the hysteresis.

The data for resistance under pressure are given in Table II. Except for the hysteresis in the transition range just discussed the results for these alloys were unusually clean cut: the curves were smooth, single valued with increasing and decreasing pressure, and with no permanent change of resistance after the initial application of pressure, that is, with no seasoning effects. Furthermore, the agreement between the resistance measurements to 30,000 and to 100,000 was unusually good, the correction for reducing the 100,000 results to agreement with those to 30,000 varying between $-6.2$ and $+6.5$ per cent, average numerical value, 4.7. In general, the effects of pressure on resistance have no unusual feature; in the middle of the composition range and at the higher pressures the decrease of resistance brought about by pressure is less than for the pure metals.

The immediate interest in the four compositions 1, 2, 98, and 99 per cent thallium was to check the previous generalization that the pressure coefficient of dilute solutions of one metal in another is greater algebraically than that of the pure metal. This rule is satisfied by the one per cent solution of indium in thallium, and also by the two per cent solution, but with less definiteness. The effects of the dissolved indium are in any event very small. At the indium rich end, on the other hand, the rule is definitely broken, the pressure coefficients of the solutions being greater numerically, not algebraically, than that of indium. The maximum effect of dissolved thallium is shown already at 0.2 per cent Tl, beyond which the trend reverses, but the coefficient of pure indium is not regained until between 5 and 10 per cent thallium. The effect of small dissolved impurity would thus seem to be far from linear. This would underline the importance of procuring as pure metals as possible for determination of pressure coefficients.

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Consider next the compressions as given in Table II. The compressibilities of pure indium and pure thallium are unusually close together, and except for the influence of the transition, the compressions of the alloys are close to those of the pure metals. The progression of values as a function of composition deviates somewhat from smoothness, but it is not certain that this is beyond experimental error. The transition was affected with capricious hysteresis and supercooling, so that it is not possible to give a unified treatment of the data. For the 23 and 8 per cent indium compositions the hysteresis limits were sufficiently narrow to justify giving a mean pressure for the transition; the figures in the table apply to one modification at lower pressures and the other modification at higher pressures. The 30 and 16.47 per cent compositions, however, showed so wide a loop that it was necessary to indicate the compressions of the two phases over a range of pressure, which in the case of 16.47 composition extended from 10,000 to 25,000 kg/cm$^2$. The magnitude of the change of volume at the transition increases in general with increasing thallium content. The increase is somewhat irregular, but an extrapolation which is as good as any other is consistent with the value 0.007 for pure thallium found in previous measurements of compression to 100,000. Again, as in the case of resistance, there would seem to be no doubt that the transition encountered here is to the room temperature, high pressure phase, and not to the high temperature atmospheric phase.

None of the shearing curves show any episode suggesting a transition, and the curves for all compositions are very closely similar, consisting of a nearly linear rise over the entire range to 80,000, with unusually small hysteresis between increasing and decreasing pressure. The absolute values of shearing strength at 80,000 for the respective compositions 80, 60, 50, 40, 30 and 16.47 indium were: 1,170, 1,240, 1,240, 1,320, 1,420 and 1,250 kg/cm$^2$.

*Thallium — Lead.* According to Hansen[6] the system at room temperature, between 0 and 80 atomic per cent thallium, consists of solid solutions. Extrapolation of the melting phenomena would suggest that these solutions exist in two phases, but the actual phenomena at room temperature and lower exhibit nothing suggesting anything else than a single homegeneous solution range up to 80 per cent thallium. Beginning in the nebulous neighbor-

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hood of 80 per cent, Hansen's diagram indicates that there is a domain of mechanical mixture extending up to within a few per cent of pure thallium, beyond which the solution is a dilute solution in thallium. Tang and Pauling[7], from X-ray measurements on eleven compositions, conclude that there is strong evidence that the ordered structures $PbTl_3$ and $PbTl_7$ exist at room temperature, and that in intermediate ranges solid solutions exist.

In this present work eleven compositions were studied: 2.5, 5, 10, 15, 20, 40, 60, 80, 95, 98, and 99 atomic per cent lead. There was no evidence of inhomogeneity in the castings, as indeed would not be expected because of the character of the melting curve. The densities are a linear function of composition within two units in the second decimal place.

The alloys are all soft and were extruded into wire for the resistance measurements to 30,000 at temperatures varying from 110° to 150°. The specific resistances should be good. In the range 15 to 100 per cent lead both specific resistance and temperature coefficient of resistance show the smooth catenary shape to be expected of a continuous series of solutions. Below 15 per cent lead, however, the regularity of the results is disturbed by the values for 2.5 per cent lead, the specific resistance of which lies high and the temperature coefficient low. There is evidently some complication in the system at low lead concentrations: one is reminded of the compound $PbTl_7$ of Tang and Pauling.

Under pressure the resistance at the thallium rich end of the series shows transition phenomena, of quite a different character from the indium – thallium series. In interpreting Table III it is to be kept in mind that the double columns of resistances for some of the compositions refer to the measurements in the 30,000 apparatus, in which a pressure cycle was described from atmospheric pressure to maximum at 30,000 and back to atmospheric again. The fact that two columns are not given for the data above 30,000 does not mean that hysteresis would not have been shown in this range also, but is merely a reflection of the fact that in the 100,000 apparatus readings could be made only with increasing pressure. The 2.5 lead composition has a drop of resistance beginning, with increasing pressure, in the neighborhood of 20,000, accelerating strongly up to 28,000, beyond which it flattens out to 30,000. On release of pressure the corresponding

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rapid down-drop begins in the neighborhood of 17,000, is nearly completed at 10,000, but the original resistance is not exactly recovered so that there is a slight permanent change of zero. At 5 per cent lead an accelerated drop begins in the neighborhood of 25,000, which has not progressed far by 30,000. On release of pressure from 30,000 there is no abrupt drop at any pressure, but the curve is smooth over its entire length, with continually decreasing pressure, down to zero pressure. This composition shows a major drop of resistance at 40,000 in the 100,000 apparatus. At 10 and 15 per cent lead the same tendency continues, now manifested by increasingly slight hysteresis between increasing and decreasing curves over their entire length up to 30,000. Since here the pressure at the initiation of the break decreases with decreasing lead content, there can be no question of the new modification being the previously known modification of pure thallium at 40,000, but some new phase or phases seems indicated. It does not seem possible that the previously known transition at atmospheric pressure at 232° can be involved here, and it would seem necessary to invoke the compound $PbTl_7$ of Tang and Pauling and ascribe to it its own pressure transition.

As far as the measurements with the 30,000 apparatus go it might be expected that the transition which apparently had been only partially initiated at 30,000 for the 5 per cent lead composition would be pushed to completion at higher pressures, where the transition should also occur for higher lead contents. This, however, did not prove to be the case except for the 5 per cent composition, but the measurements to 100,000 showed no transition for lead contents of 20 per cent or higher, although showing it for the two lower contents. That is, the transition simply fades out of the picture. This is not inconsistent with the existence of the compound $PbTl_3$ of Tang and Pauling.

Reduction of the readings with the 100,000 apparatus to secure agreement with the 30,000 readings is affected with considerable uncertainty for the 2.5 and 5 per cent lead compositions because of the hysteresis in the 30,000 readings. The 100,000 readings were adjusted in a not altogether simple manner according to methods suggested by my previous experience, and the details will not be elaborated. For the 2.5 composition the maximum correction was +38 per cent, shading off at higher pressures,

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# TABLE III

## Thallium — Lead System

| | 100 Tl | 97.5 Tl 2.5 Pb | 95 Tl 5 Pb | 90 Tl 10 Pb | 85 Tl 15 Pb | 80 Tl 20 Pb |
|---|---|---|---|---|---|---|
| Density | 11.86 | 11.83 | 11.86 | 11.80 | 11.79 | 11.74 |
| $\rho_{00} \times 10^6$ | 16.9 | 20.3 | 18.3 | 18.8 | 19.7 | 22.8 |
| Temperature Coefficient | .00434 | .00359 | .00353 | .00314 | .00274 | .00239 |
| **Pressure** kg/cm² | | | Rp/Ro | | | |
| 0 | 1.000 | 1.000 .997 | 1.000 .995 | 1.000 .996 | 1.000 .998 | 1.000 |
| 5,000 | .936 | .941 .938 | .939 .934 | .943 .938 | .949 .947 | .957 |
| 10,000 | .882 | .892 .878 | .888 .879 | .894 .888 | .905 .903 | .921 |
| 15,000 | .832 | .848 .741 | .843 .831 | .860 .853 | .868 .866 | .889 |
| 20,000 | .795 | .805 .602 | .803 .787 | .816 .807 | .836 .834 | .861 |
| 25,000 | .760 | .615 .560 | .767 .749 | .783 .775 | .808 .806 | .836 |
| 30,000 | .727 | .526 | .714 | .745 | .780 | .814 |
| | {.665 | | {.642 | | | |
| 40,000 | {.487 | .471 | {.526 | .681 | .737 | .776 |
| 50,000 | .436 | .427 | .479 | .626 | .701 | .744 |
| 60,000 | .391 | .392 | .443 | .582 | .669 | .720 |
| 70,000 | .352 | .367 | .411 | .551 | .644 | .697 |
| 80,000 | .319 | .348 | .384 | .522 | .622 | .679 |
| 90,000 | .290 | .334 | .361 | .495 | .602 | .662 |
| 100,000 | .265 | .318 | .341 | .472 | .585 | .650 |
| | | | $-\Delta V/Vo$ | | | |
| 5,000 | .0137 | .0137 | .0138 | .0135 | .0133 | .0135 |
| 10,000 | .0263 | .0260 | .0259 | .0257 | .0252 | .0255 |
| 15,000 | .0379 | .0372 .0423 | .0373 | .0369 | .0364 | .0366 |
| 20,000 | .0484 | .0476 .0528 | .0472 | .0474 | .0443 | .0469 |
| 25,000 | .0587 | .0623 | .0567 | .0568 | .0556 | .0565 |
| | | | {.0646 | {.0654 | | |
| 30,000 | .0684 | .0713 | {.0670 | .0666 | .0639 | .0655 |
| 35,000 | .0775 | .0798 | .0759 | .0745 | .0722 | .0738 |
| 40,000 | .0859 | .0868 | .0842 | .0815 | .0796 | .0824 |

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## TABLE III – *Continued*

### THALLIUM – LEAD SYSTEM

| 60 Tl 40 Pb | 40 Tl 60 Pb | 20 Tl 80 Pb | 5 Tl 95 Pb | 2 Tl 98 Pb | 1 Tl 99 Pb | 100 Pb | |
|---|---|---|---|---|---|---|---|
| 11.62 | 11.52 | 11.44 | 11.35 | 11.34 | 11.34 | 11.35 | Density |
| 35.8 | 35.9 | 29.7 | 22.7 | 20.6 | 20.4 | 19.1 | $\rho_{00} \times 10^6$ |
| .00168 | .00190 | .00249 | .00350 | .00383 | .00394 | .00421 | Temperature Coefficient |
| | | | Rp/Ro | | | | Pressure kg/cm² |
| 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 0 |
| .958 | .949 | .945 | .935 | .935 | .936 | .932 | 5,000 |
| .922 | .907 | .898 | .882 | .878 | .878 | .875 | 10,000 |
| .888 | .870 | .856 | .837 | .830 | .829 | .825 | 15,000 |
| .859 | .836 | .820 | .797 | .789 | .785 | .782 | 20,000 |
| .832 | .810 | .787 | .760 | .752 | .747 | .743 | 25,000 |
| .808 | .779 | .759 | .728 | .718 | .713 | .708 | 30,000 |
| .762 | .732 | .709 | .671 | | | .651 | 40,000 |
| .728 | .690 | .669 | .624 | | | .606 | 50,000 |
| .697 | .656 | .635 | .584 | | | .573 | 60,000 |
| .673 | .627 | .607 | .552 | | | .546 | 70,000 |
| .651 | .602 | .581 | .523 | | | .524 | 80,000 |
| .635 | .581 | .558 | .499<br>.493 (?) | | | .505 | 90,000 |
| .622 | .560 | .539 | .472 | | | .490 | 100,000 |
| | | | $-\Delta V/Vo$ | | | | |
| .0122 | .0129 | .0118 | | | | .0118 | 5,000 |
| .0236 | .0242 | .0223 | | | | .0224 | 10,000 |
| .0347 | .0348 | .0326 | | | | .0323 | 15,000 |
| .0451 | .0448 | .0423 | | | | .0414 | 20,000 |
| .0547 | .0542 | .0518 | | | | .0499 | 25,000 |
| .0637 | .0631 | .0606 | | | | .0579 | 30,000 |
| .0724 | .0716 | .0687 | | | | .0650 | 35,000 |
| .0807 | .0797 | .0764 | | | | .0718 | 40,000 |

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and for the 5 per cent composition also +38, again shading off. The corrections for the other compositions were, in order: +38, +31, +12, +18, +28, +19, and +30, all constant over the pressure range. At the lead rich end of the series the variation of the pressure coefficient is in accordance with expectations for a solution, the coefficient becoming algebraically greater with increasing thallium content. At the thallium end the phase transition with accompanying hysteresis obscures the answer to the question. At the lead rich end of the series attention is to be called to a not entirely certain small jump in resistance at 90,000 kg/cm$^2$ for the 95 Pb – 5 Tl composition.

Next consider the compressions as given in Table III. The evidence of a new phase at low lead content is confirmed by the volumes, the volume discontinuity shifting to higher pressures with increasing lead content and becoming less in magnitude. That is, again the transition fades out. At the lead rich end the compressions of the alloys are greater than that of pure lead, and increase with thallium content.

With one exception the shearing curves are all very much alike and with no episode certainly beyond experimental error. The shearing strengths of pure lead and pure thallium are nearly the same, being respectively 1,150 and 1,180 kg/cm$^2$ at 80,000 kg/cm$^2$. There is a slight episode, an accelerated rise, for pure thallium corresponding to the known transition at 40,000, but it is very minor, not at all like the discontinuity of resistance or volume. The other compositions do not show this episode at all. The curves are nearly linear, with little hysteresis, sometimes with slight upward and sometimes with slight downward curvature, and with shearing strengths at 80,000 varying from 1,080 to 1,480 (the latter at 20 per cent lead). The shearing curve for 95 Pb – 5 Tl, which was carried to 100,000, has a small rise in the neighborhood of 80,000, confirming the possibility of a new phase shown by the resistance.

The shearing curve for 40 per cent lead is markedly exceptional. This has a maximum at 40,000 and minimum at 50,000, confirmed on release of pressure, with an extreme shearing strength at 80,000 of only 720 kg/cm$^2$, the lowest value observed at this pressure for any substance. Since the composition 20 per cent lead did not show this anomoly it is probable that the com-

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pound $PbTl_3$ of Tang and Pauling is not involved in this phenomenon, and again the hypothesis of a polymorphic modification produced by shearing stress as distinguished from hydrostatic pressure seems necessary to account for the effect.

*Thallium – Tin.* According to Hansen[3] the system consists at room temperature of a solution of tin in thallium in the range from 0 per cent to something in the general neighborhood of 20 atomic per cent tin, and for the rest of the range to pure tin a mechanical mixture of pure tin and the limiting solid solution, there being no detectible solubility of thallium in tin.

In the present work eleven compositions were studied: 0.99, 2.5, 3.7, 5, 7.5, 10, 15, 20, 40, 60, and 80 atomic per cent tin, the majority of the compositions thus being in the range of supposed solid solution. The densities are nearly a linear function of composition over the entire range, the maximum deviation from linearity being about plus 1 per cent at mid range. This linearity is of special significance in view of the large difference of density between the pure components. There is no evidence of difference of density between different parts of the same casting, so that the homogeneity is doubtless adequate, as would be expected from the shape of the melting curve.

The alloys are all soft and the resistance measurements to 30,000 were made on wires extruded at temperatures from 110° to 130°. Specific resistance, shown in Figure 2, in the domain 0 to 20 per cent tin increases by a large amount, as would be expected of a solution, but the increase is not smooth, the first small additions of tin being accompanied by a disproportionally large increase of resistance, after which there is a slight dropping off to 10 per cent tin, where there is a sharp upturn to a sharp maximum at 20 per cent tin. It would seem highly probable that the interval out to 20 per cent tin is more complex than a simple solution, with perhaps a compound in the neighborhood of 10 per cent. From 20 to 100 per cent tin resistance falls off, approximately, but definitely not, linearly, in a way roughly consistent with a mechanical mixture in this domain. The temperature coefficient of resistance drops steeply with composition in the 0 to 20 per cent tin range, with some irregularities, which, however, are much smaller than those of the specific resistance in the same range. Beyond 20 per cent tin the temperature coeffi-

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cient rises in a way not inconsistent with the diagram of Hansen.

The transition phenomena in this series are entirely confined to the thallium rich end, there being no evidence for a transition from either resistance or compression from the composition 10 per cent tin and higher. In the range up to 10 per cent tin the transition phenomena are not sharp. There is much rounding of the corners of the transition, the appearance of which is irregular and not always the same as shown by the resistance and compression data. One generalization can be made from both the

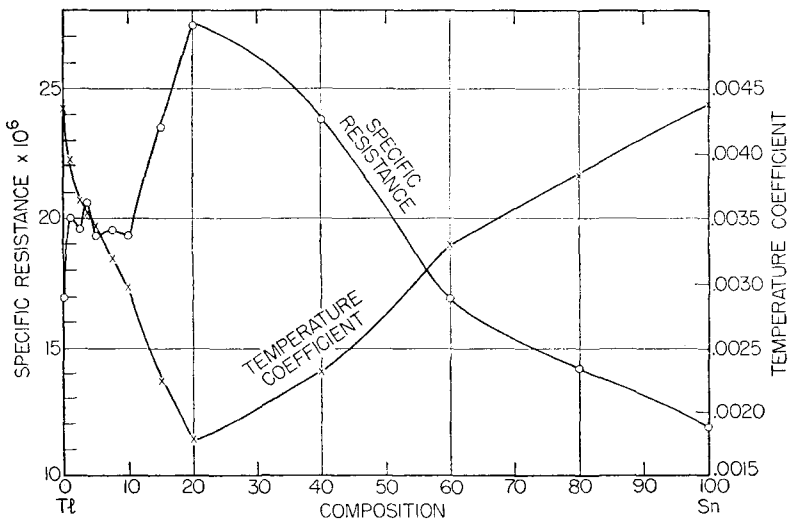


Figure 2. Specific resistance and temperature coefficient of resistance at atmospheric pressure of the thallium — tin system as a function of composition in atomic per cent.

resistance and the volume measurements, namely that the addition of small amounts of tin smears out the thallium transition in the direction of lower pressures. The resistance of the 0.99 tin composition shows no premonition of the transition up to 30,000, the readings in the 30,000 apparatus being without creep and single valued. With this composition a discontinuity of resistance shows up in the 100,000 apparatus in the neighborhood of 40,000, and is so shown in Table IV. The transition of this

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composition shown in the volume apparatus occurs between 25,000 and 35,000, and is apparently complete at 40,000. The next three compositions, 2.5, 3.7 and 5 tin, show the initiation and partial running of the transition in the 30,000 apparatus, there being definite hysteresis between the readings with increasing and decreasing pressure with some permanent change of zero. At none of these compositions, however, is 30,000 sufficient to complete the transition, but the major jump down in resistance shows up in the 100,000 apparatus, smeared over a region centering somewhere between 30,000 and 40,000. The amount of hysteresis in the 30,000 apparatus is not regular, being greatest for the 2.5 Sn composition. The measurements of compression in general show the transition confined within somewhat narrower limits than the resistance measurements, the center of gravity of the region of transition shifting to lower pressures with increasing tin content. The volume discontinuity at the transition becomes smaller with increasing tin content, but not with regularity, and apparently would vanish not far above 7.5 per cent tin. This latter composition shows no hysteresis of resistance in the 30,000 apparatus, the transition in the resistance appearing only in the 100,000 apparatus. Consistently with this the transition in the compression appeared with increasing pressure only above 30,000, but with decreasing pressure was smeared out down to nearly 10,000.

Although the resistance of the 7.5 per cent tin composition is shown single valued in the table, there was, immediately after release of pressure, a depression of the zero of resistance by 0.38 per cent. There was practically complete recovery of the initial zero after 14 hours at room temperature. Effects of this sort remained perceptible up to 40 per cent tin, but were too small to show in the table.

The resistance measurements in the 100,000 apparatus and the compression measurements on the compositions 0.99 and 3.7 per cent tin were made several months after the others and after the casting of the samples. These two specimens therefore had opportunity to approach internal equilibrium more closely than the others. The table does indeed show departures from the regular sequence of values which possibly are due to this effect.

Above and including 10 per cent tin all trace of any transition

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# TABLE IV

## Thallium – Tin System

| | 100 Tl | 99.01 Tl .99 Sn | 97.5 Tl 2.5 Sn | 96.3 Tl 3.7 Sn | 95 Tl 5 Sn | 92.5 Tl 7.5 Sn |
|---|---|---|---|---|---|---|
| Density | 11.86 | 11.79 | 11.75 | 11.70 | 11.66 | 11.56 |
| $\rho_{00} \times 10^6$ | 16.9 | 20.0 | 19.6 | 20.6 | 19.3 | 19.5 |
| Temperature Coefficient | .00434 | .00395 | .00364 | .00355 | .00343 | .00318 |
| Pressure kg/cm² | | | | $R_P/R_0$ | | |
| 0 | 1.000 | 1.000 | 1.000 .987 | 1.000 .993 | 1.000 .989 | 1.000 |
| 5,000 | .936 | .939 | .940 .925 | .938 .932 | .937 .924 | .937 |
| 10,000 | .882 | .888 | .889 .871 | .888 .880 | .886 .871 | .885 |
| 15,000 | .832 | .844 | .844 .799 | .842 .835 | .841 .822 | .839 |
| 20,000 | .795 | .805 | .804 .690 | .803 .792 | .802 .774 | .803 |
| 25,000 | .760 | .770 | .756 .612 | .766 .741 | .765 .735 | .766 |
| 30,000 | .727 | .739 | .739<br>.605 | .704 | .735<br>.606 | .736 |
| | .665 | .695 | | .660 | | .692 |
| 40,000 | .487 | .583 | .567 | .627 | .570 | .640 |
| 50,000 | .436 | .548 | .532 | .597 | .538 | .612 |
| 60,000 | .391 | .515 | .502 | .571 | .508 | .587 |
| 70,000 | .352 | .488 | .476 | .550 | .481 | .564 |
| | | | | .533 | | |
| 80,000 | .319 | .466 | .453 | .529 | .460 | .544 |
| 90,000 | .290 | .445 | .431 | .511 | .445 | .528 |
| 100,000 | .265 | .427 | .413 | .494 | .419 | .512 |
| | | | | $-\Delta V/V_0$ | | |
| 5,000 | .0137 | .0132 | .0137 | .0133 | .0162 | .0133 |
| 10,000 | .0263 | .0255 | .0262 | .0259 | .0284 | .0252 |
| 15,000 | .0379 | .0368 | .0376 | .0367 | .0397 | .0361 .0377 |
| | | | .0483 | | | |
| 20,000 | .0484 | .0474 | .0520 | .0471 .0512 | .0501 | .0464 .0481 |
| 25,000 | .0587 | .0575 .0634 | .0620 | .0569 .0609 | .0595 | .0562 .0579 |
| 30,000 | .0684 | .0668 .0735 | .0710 | .0662 .0701 | .0718 [a] | .0650 .0669 |
| 35,000 | .0775 | .0754 .0825 | .0794 | .0774 .0807 | .0798 | .0755 |
| 40,000 | .0859 | .0911 | .0872 | .0902 | .0871 | .0837 |

(a) Transition at 27,250. Volumes .0634 and .0672.

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## TABLE IV – *Continued*

### Thallium – Tin System

| 90 Tl 10 Sn | 85 Tl 15 Sn | 80 Tl 20 Sn | 60 Tl 40 Sn | 40 Tl 60 Sn | 20 Tl 80 Sn | 100 Sn | |
|---|---|---|---|---|---|---|---|
| 11.48 | 11.23 | 10.98 | 10.14 | 9.17 | 8.24 | 7.29 | Density |
| 19.3 | 23.5 | 27.4 | 23.8 | 16.9 | 14.2 | 11.9 | $\rho_{(0)} \times 10^6$ |
| .00296 | .00225 | .00178 | .00232 | .00330 | .00383 | .00438 | Temperature Coefficient |
| | | | $R_p/R_0$ | | | | Pressure kg/cm² |
| 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 0 |
| .937 | .948 | .954 | .955 | .950 | .950 | .951 | 5,000 |
| .885 | .905 | .913 | .914 | .908 | .908 | .908 | 10,000 |
| .840 | .868 | .879 | .878 | .871 | .870 | .870 | 15,000 |
| .803 | .836 | .848 | .846 | .839 | .836 | .834 | 20,000 |
| .769 | .808 | .822 | .817 | .810 | .805 | .803 | 25,000 |
| .741 | .783 | .798 | .791 | .782 | .777 | .775 | 30,000 |
| .696 | .741 | .756 | .745 | .738 | .728 | .724 | 40,000 |
| .660 | .709 | .722 | .708 | .701 | .689 | .683 | 50,000 |
| .632 | .680 | .694 | .676 | .669 | .656 | .647 | 60,000 |
| .608 | .657 | .670 | .652 | .642 | .629 | .618 | 70,000 |
| .588 | .637 | .648 | .627 | .619 | .605 | .592 | 80,000 |
| .570 | .618 | .628 | .607 | .598 | .582 | .569 | 90,000 |
| .554 | .600 | .609 | .586 | .578 | .562 | .548 | 100,000 |
| | | | $-\Delta V/V_0$ | | | | |
| .0134 | .0135 | .0130 | .0112 | .0114 | .0101 | .0099 | 5,000 |
| .0257 | .0253 | .0249 | .0219 | .0214 | .0198 | .0184 | 10,000 |
| .0363 | .0361 | .0354 | .0321 | .0310 | .0281 | .0265 | 15,000 |
| .0463 | .0462 | .0456 | .0418 | .0402 | .0366 | .0342 | 20,000 |
| .0558 | .0557 | .0553 | .0509 | .0486 | .0450 | .0417 | 25,000 |
| .0642 | .0643 | .0643 | .0596 | .0564 | .0528 | .0488 | 30,000 |
| .0718 | .0723 | .0726 | .0679 | .0641 | .0598 | .0548 | 35,000 |
| .0789 | .0795 | .0804 | .0754 | .0712 | .0657 | .0610 | 40,000 |

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has disappeared from both resistance and volume phenomena. The sequence of numerical values is not monotonic between 10 and 100 per cent tin, however, but both resistance and compression show some sort of turning point at 20 per cent tin. This composition is also the composition of maximum specific resistance, and doubtless marks some sort of landmark in the structure.

Unlike the system thallium – lead the transition out to 10 per cent tin is doubtless the regular high pressure thallium transition, smeared out and depressed to lower pressures by the addition of tin. The failure of exact parallelism between resistance and volume phenomena may well be a result of the different geometry in the two cases, it being much easier for the transition to run only partially in isolated parts of the long slender resistance specimen than in the chunky compression specimen. The disappearance of the transition beyond 10 per cent tin suggests, as does also the turning point in the specific resistance, that 10 per cent approximately marks a new phase, and that below 10 per cent the system is a solution of pure thallium and the new phase. One is reminded of the phase $PbTl_7$ found by Tang and Pauling, but this cannot be exactly it. Furthermore, the new phase in the tin – thallium system does not have an independent high pressure transition, as it did in the lead – thallium system.

Beyond 10 per cent tin and up to the general neighborhood of 20 per cent, both the pressure phenomena and the specific resistance suggest a mixture with still another new phase, perhaps analogous to the $PbTl_3$ of Tang and Pauling, but probably not exactly it.

The shearing phenomena are very similar to those for the series lead – thallium. With a single exception the curves are nearly linear, with little hysteresis, and only slight curvature in either direction. The exception occurs at the composition 40 per cent tin, where there is a well marked point of inflection, an episode not so well marked as the maximum and minimum at the same composition in the lead – thallium series, but unmistakable, and also setting this composition off apart from the others as regards shearing phenomena. The shearing strengths at 80,000 for the compositions 2.5, 5, 10, 15, 20, 40, 60 and 80 tin were respectively: 1,100, 1,040, 1,050, 1,120, 1,500, 1,150, 1,580 and 1,470 kg/cm$^2$. Again the exceptional composition has a shearing strength, 1,150,

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well below those on either side, and again a polymorphic transition under shearing stress seems indicated.

*Thallium — Bismuth.* Hansen's melting diagram[9] shows three eutectic cusps and two maxima, and therefore presumably at least two homogeneous ranges between the pure components. However, except in the neighborhood of pure thallium, no equilibrium points have been determined below 188°. The indications are that the attainment of equilibrium at low temperatures is very sluggish and therefore the material ill defined. Hansen's diagram suggests at room temperature a domain of mixed bismuth and delta reaching to 35 per cent Tl, a homogeneous domain of delta from 35 to 45 per cent Tl, a region of mixed delta and gamma from 45 to 65 per cent Tl, a homogeneous domain of gamma from 70 to 92 per cent Tl, and from 92 to 100 Tl domains, not well established, of the beta and alpha (high and low temperature) lattices of pure Tl and a mixture of beta and gamma.

In this work attention was concentrated on the bismuth rich and the thallium rich ends of the series, only seven intermediate compositions being investigated. In all, 16 compositions were studied: 0.5, 1.0, 1.25, 1.5, 1.75, 2, 5, 10, 20, 50, 60, 70, 80, 90, 98, and 99 atomic per cent bismuth. The principal interest was in the behavior of dilute solutions of thallium in bismuth, and of dilute solutions of bismuth in thallium. Hansen's diagram indicates no solubility of thallium in bismuth, but solubility of bismuth in alpha (low temperature) thallium up to perhaps 10 per cent. At the bismuth rich end the questions of interest were whether dilution of bismuth with thallium would produce the enormous effects found for tin and lead (the latter to be published in the fourth paper of this series), and whether new compounds are formed. At the thallium rich end it was of particular interest to find whether the effect of dissolved bismuth on the thallium transition is the same as the effect of dissolved tin or lead. At intermediate compositions it was of interest to find whether the new phases show any of the transitions of pure bismuth or thallium. It is to be remarked that the atomic radii of bismuth and thallium in the solid state are unusually close, being 1.52 and 1.55 A respectively, so that for this reason simple effects are to be expected on mixing the two metals. If, however, compounds

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# TABLE V

## Thallium — Bismuth System

| | | 100 Tl | 99.5 Tl 0.5 Bi | 99 Tl 1 Bi | 98.75 Tl 1.25 Bi | 98.5 Tl 1.5 Bi | 98.25 Tl 1.75 Bi | 98 Tl 2 Bi | 95 Tl 5 Bi | 90 Tl 10 Bi | 80 Tl 20 Bi |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Density | | 11.86 | 11.85 | 11.84 | 11.83 | 11.82 | 11.80 | 11.81 | 11.81 | 11.70 | 11.45 |
| $\rho_{00} \times 10^6$ | Before | 16.9 | 19.6 | 21.7 | 21.2 | 21.9 | 22.5 | 21.2 | 24.3 | 38.0 | 64.4 |
| | After | | 19.6 | 21.7 | 21.2 | 21.5 | 22.1 | 21.1 | 24.3 | 38.0 | 64.4 |
| Temperature Coefficient | Before | | | | | | | | | | |
| | After | .00434 | .00376 | .00345 | .00348 | .00331 | .00328 | .00334 | .00259 | .00141 | .00086 |
| Pressure kg/cm² | | | | | | Rp/Ro | | | | | |
| 0 | | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 |
| 5,000 | | .936 | .940 | .945 | .945 | .945 | .943 | .946 | .950 | .969 | .970 |
| 10,000 | | .882 | .891 | .897 | .898 | .896 | .897 | .898 | .909 | .942 | .944 |
| 15,000 | | .832 | .848 | .856 | .857 | .854 | .858 | .857 | .875 | .919 | .919 |
| 20,000 | | .795 | .811 | .820 | .821 | .816 | .822 | .820 | .845 | .898 | .898 |
| 25,000 | | .760 | .778 | .783 / .589 | .787 | .780 | .788 | .782 | .818 | .880 | .878 |
| 30,000 | | .727 | .748 | .552 | .760 | .753 | .763 | .754 | .794 | .863 | .859 |
| 40,000 | | .665 / .487 | .696 / .471 | .493 | .713 | .702 | .713 | .700 | .752 | .834 | .826 |
| 50,000 | | .436 | .437 | .447 | .674 / .507 | .658 / .451 | .668 / .495 | .654 / .479 | .717 / .676 | .810 | .800 |
| 60,000 | | .391 | .405 | .410 | .469 | .415 | .464 | .440 | .648 | .788 | .778 |
| 70,000 | | .352 | .377 | .382 | .438 | .382 | .436 | .406 | .626 | .770 | .759 |
| 80,000 | | .319 | .352 | .362 | .412 | .353 | .412 | .380 | .607 | .754 | .742 |
| 90,000 | | .290 | .331 | .342 | .390 | .327 | .390 | .359 | .589 | .740 | .727 |
| 100,000 | | .265 | .312 | .325 | .371 | .305 | .370 | .339 | .572 | .727 | .714 |
| | | | | | | $-\Delta V/V_0$ | | | | | |
| 5,000 | | .0137 | .0132 | .0147 | .0139 | .0135 | .0135 | .0133 | | | .0132 |
| 10,000 | | .0263 | .0258 | .0270 | .0267 | .0259 | .0261 | .0256 | | | .0254 |
| 15,000 | | .0379 | .0372 | .0384 | .0384 | .0373 | .0424 [e] | .0400 [f] | | | .0367 |
| 20,000 | | .0484 | .0477 | .0492 | .0484 | .0537 [d] | .0533 | .0506 | | | .0474 |
| 25,000 | | .0587 | .0576 | .0652 [b] | .0648 [c] | .0638 | .0635 | .0612 | | | .0578 |
| 30,000 | | .0684 | .0675 | .0746 | .0745 | .0736 | .0730 | .0709 | | | .0672 |
| 35,000 | | .0775 | .0816 [a] | .0842 | .0837 | .0827 | .0819 | .0808 | | | .0756 |
| 40,000 | | .0859 | .0908 | .0921 | .0919 | .0907 | .0906 | .0904 | | | .0835 |

(a) Transition at 30,220. Volumes .0679 and .0734.
(b) Transition at 23,540. Volumes .0570 and .0624.
(c) Transition at 20,830. Volumes .0510 and .0563.
(d) Transition at 17,360. Volumes .0420 and .0481.
(e) Transition at 14,900. Volumes .0374 and .0422.
(f) Transition at 11,940. Volumes .0301 and .0328.

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## TABLE V — *Continued*

### Thallium — Bismuth System

| | | 50 Tl 50 Bi | 40 Tl 60 Bi | 30 Tl 70 Bi | 20 Tl 80 Bi | 10 Tl 90 Bi | 2 Tl 98 Bi | 1 Tl 99 Bi | 100 Bi |
|---|---|---|---|---|---|---|---|---|---|
| Density | | 11.06 | 10.91 | 10.77 | 10.42 | 10.14 | 9.87 | 9.83 | 9.81 |
| $\rho_{00} \times 10^6$ | Before | | 66.8 | 56.9 ± | 78.3 | 113.6 | 149.5 | 142.2 | 131 |
| | After | 82.6 | 66.8 | 56.2 ± | 73.2 | 89.4 | 138.1 | 134.5 | 126 |
| Temperature Coefficient | Before | | | | .00261 | .00177 | | .00207 | .00331 |
| | After | .00131 | .00218 | | .00296 | .00311 | .00117 | .00181 | .00326 |
| Pressure kg/cm² | | | | | Rp/Ro | | | | |
| 0 | | 1.000 | 1.000 | 1.000 .987 .992 | 1.000 .932 | 1.000 .830 .844 | 1.000 .923 | 1.000 .948 | 1.000 |
| 5,000 | | .939 | .925 | .920 .898 | .958 .892 | 1.002 .846 | 1.086 1.021 | 1.107 1.054 | 1.098 |
| 10,000 | | .891 | .863 | .859 .785 | .916 .789 | 1.003 .822 | 1.193 1.114 | 1.234 1.145 | 1.210 |
| 15,000 | | .849 | .812 | .806 .731 | .882 .725 | .999 .803 | 1.288 1.209 | 1.370 1.280 | 1.335 |
| 20,000 | | .813 | .770 | .761 .687 | .849 .704 | .990 .800 | 1.410 1.286 | 1.518 1.393 | 1.474 |
| 25,000 | | .784 | .735 | .720 .598III | .818 | .973 .185II | 1.506 .175 1.344 | 1.660 .180 1.479 | 1.638 |
| 30,000 | | .755 | .703 | .611III | .552 (g) | .506III | .450 | .478 | .900 |
| 40,000 | | .710 | .654 | .583 | .528 | .486 | .423 | | .867 |
| 50,000 | | .672 | .613 | .561 | .505 | .465 | .402 | | .837 |
| 60,000 | | .640 | .579 | .539 | .485 | .448 | .387 | | .811 |
| 70,000 | | .615 | .551 | .521 | .468 | .434 | .375 | | .787 |
| 80,000 | | .593 | .528 | .504 | .453 | .421 | .365 | | .764 |
| 90,000 | | .573 | .507 | .489 | .441 | .409 | .357 | | .747 |
| 100,000 | | .556 | .489 | .475 | .431 | .399 | .349 | | .730 |
| | | | | | $-\Delta V/Vo$ | | | | |
| 5,000 | | .0140 | .0135 | .0134 | .0132 | .0144 | | | .0163 |
| 10,000 | | .0262 | .0256 | .0246 | .0256 | .0275 | | | .0290 |
| 15,000 | | .0375 | .0367 | .0365 | .0370 | .0390 | | | .0410 |
| 20,000 | | .0477 | .0470 | .0470 | .0477 | .0499 | | | .0520 |
| 25,000 | | .0572 | .0568 | .0573I .0674III | (h) | (i) | | | |
| 30,000 | | .0658 | .0656 | .0664I .0771III | .1040 | .1296 | | | .1526 |
| 35,000 | | .0741 | .0736 | .0864 | .1121 | .1381 | | | .1601 |
| 40,000 | | .0818 | .0811 | .0946 | .1188 | .1455 | | | .1670 |

(g) Resistance of II at 20,000, 0.406.

(h) Volumes of I, II, and III at 25,000: .0579, .0788, .0946.

(i) Volumes of I, II, and III at 25,000: .0602, .0959, .1201.

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are formed and the dilute solutions are solutions of molecules of compound in atoms of pure components, more complicated effects would be expected.

The alloys were prepared in pyrex tubing ¼ inch in inside diameter. As usual, the weighed components were placed in the tube, which was evacuated and sealed. The contents were melted in an electric furnace held somewhat above the melting point. The tube was then shaken violently to thoroughly mix, and quenched immediately by plunging into a silicone oil at room temperature. The thermal shock of this procedure was not sufficient to crack the glass. In this way homogeneous castings should have been obtained. It was checked that there was no perceptible difference of density between top and bottom of the casting of the 50 – 50 composition.

Density as a function of composition is shown in Figure 3. Several distinct ranges are recognizable: from 0 to 30 per cent Tl,

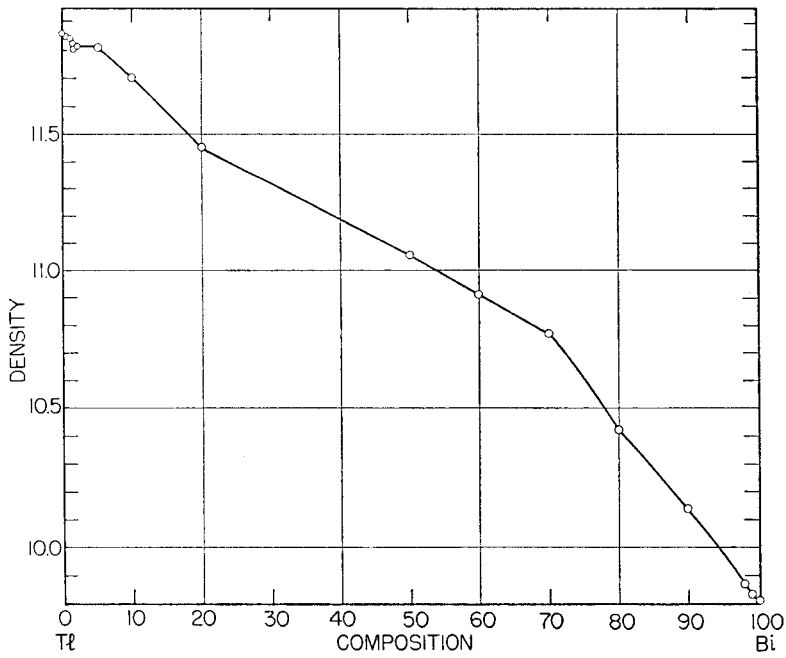


Figure 3. Density at atmospheric pressure of the thallium – bismuth system as a function of composition in atomic per cent.

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from 30 to 80 per cent, from 80 to 95, from 95 to 98, and from 98 to 100. The curve of density gives no evidence of any solubility of thallium in bismuth; this is consistent with Hansen's diagram. At the thallium rich end the stretch from 98 to 100 is consistent with solubility of bismuth in the alpha (low temperature) phase of thallium, as indicated by Hansen, and the stretch from 95 to 98, known only through its end points, perhaps covers the replacement of alpha by beta, and the replacement in turn of beta by Hansen's gamma. The stretch from 80 to 95 could be Hansen's homogeneous domain of the gamma phase. The curve of density does not suggest any break in direction, as might be anticipated from Hansen, on passing from the domain of homogeneous gamma to the domain of mixed gamma and delta.

The alloys were all soft and specimens were prepared for the resistance measurements by extrusion at moderately elevated temperatures or at room temperature. Specific resistance and temperature coefficient at atmospheric pressure are shown in Figure 4 and Table V. In the domain up to 30 per cent Tl the same phenomenon is shown as is shown by other bismuth alloys,

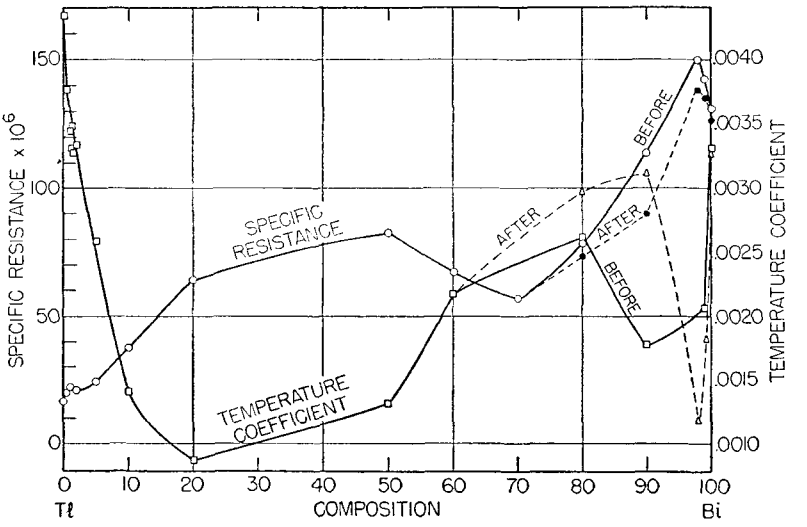


Figure 4. Specific resistance and temperature coefficient of resistance at atmospheric pressure of the system thallium – bismuth as a function of composition in atomic per cent.

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namely a permanent change of resistance after exposure to pressure. In this region two values are necessary for specific resistance and temperature coefficient, namely the values before and after exposure to 30,000 kg/cm$^2$. It is evident from Figure 4 that the electrical parameters give more information than the density. There seems to be limited but definite solubility of thallium in bismuth, the specific resistances for 1 and 2 per cent Tl being higher than that of pure bismuth and the temperature coefficients markedly lower. Furthermore, there is a break in direction of both curves at 50 per cent Tl corresponding to the transition from the domain of Hansen's homogeneous delta to mixed delta and gamma. At the thallium rich end the electrical data are not inconsistent with Hansen's diagram or with the curve of density, but the electrical episodes are perhaps not as well marked as might be expected from the curve of density.

The domain up to 30 per cent thallium is, under the action of pressure, one of incomplete internal equilibrium in which resistance may drift for a long time after a change of pressure, so that only a rough picture can be given of the state of affairs. Not only are there two transitions of bismuth in this region, but there is also the irreversible formation of perhaps a new compound, which itself has sluggish transitions under pressure. Beyond 30 per cent Tl all these complications drop out of the picture, and up to 95 per cent Tl resistance is a smooth single valued function of pressure. From 98 to 100 per cent Tl new complications appear, connected with one or the other of the thallium transitions, and resistance again is not single valued and internal equilibrium is uncertain.

Consider now the effects of pressure on resistance in detail. The resistance of the composition 1 per cent Tl behaves much like that of pure bismuth: with increasing pressure resistance increases with upward curvature, which diminishes toward 25,000. The transitions to the II and III modifications of bismuth are well marked and reversible with decreasing pressure. Below 25,000, however, the resistance with decreasing pressure falls below that with increasing pressure, and the curvature is differently distributed, there being a point of inflection near 15,000. At no pressure for this composition does the resistance creep in time after change of pressure. The composition 2 per cent Tl

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is similar, but with the beginning of progressive change. On increase of pressure curvature is at first upward, but there is a point of inflection near 10,000. The resistances at the two bismuth transitions are as before single valued and reversible. Below 25,000 the permanent decrease of resistance as compared with increasing pressure is more marked than for the 1 per cent composition, and a second slight abnormality of curvature appears at the final zero. Again all readings are steady in time with no creep. Permanent alteration in resistance on release of pressure is also shown by pure bismuth, but to a smaller extent, and is probably to be explained by failure to recover the original crystalline orientation, bismuth being strongly non-isotropic, so that grain size and orientation are important factors. In the present case of the 1 and 2 per cent solutions of thallium a second factor appears to produce a permanent change of resistance, namely the irreversible transformation to a compound or other phase which is characteristic of several bismuth alloys and which, in the case of the present thallium alloys, becomes much more prominent at higher thallium concentrations. It would be difficult to say how much of the present permanent change of resistance is due to this factor of irreversible compound formation, but it cannot be large, or creep effects would have been detectible. It is also to be commented that although the specific resistances of both 1 and 2 per cent compositions were greater than that of pure bismuth the increase is comparatively minor, being only 13 per cent for the 2 per cent composition, compared with increases by a factor of five or six in the bismuth — tin and bismuth — lead series. In the case of the tin and lead solutions the maximum increase of resistance occurs at very low concentrations of a fraction of a per cent, whereas here it would presumably occur near several per cent, the increase of resistance with composition being approximately linear with composition in the range 1 to 2 per cent. Another point is that the initial pressure coefficients of these two thallium compositions are not far from that of pure bismuth, the coefficient of the 1 per cent composition being somewhat greater and that of the 2 per cent solution somewhat less. In the case of the tin and lead solutions much larger increases of pressure coefficient were found at low concentrations.

Consider next the three compositions 10, 20, and 30 per cent

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thallium. Over this range the two bismuth transitions occur and also the irreversible compound formation and its transitions. The compound does not want to appear until pressures on the virgin material reach the neighborhood of 25,000, which is also the pressure of the transition of bismuth to modification II. Furthermore, since resistance drops during formation of compound, it is difficult to disentangle it from the bismuth transition and to decide what part of the creep observed over much of the pressure range is due to compound formation or to rounding of the corners of the bismuth transition by dissolved thallium. The compound will apparently form sluggishly at pressures as low as 20,000; at this pressure for the 10 per cent composition a drop of resistance of 0.6 per cent was observed in 100 minutes. For the other two compositions and pressures below 25,000 readings were made at intervals of five or ten minutes, an interval too short to permit isolating true creep from the temperature effects of dissipation of the heat of compression. The first increase of pressure to the neighborhood of 26,000 on the 10, 20, and 30 compositions produces a large decrease of resistance associated with the bismuth II modification. Further increase to 28,000 produces III with abrupt rise of resistance. Further increase to 30,000 produces a slight decrease, the normal effect of pressure on this phase, with no creep or other indication of incomplete internal equilibrium. On release of pressure from 30,000 to 27,000 the rising curve is retraced. On further release to the neighborhood of 25,000, the reverse transition to II occurs. This transition is inclined to be sluggish, with creep and rounding of the corners. The jumps of resistance at the I – II and II – III transitions become progressively less with increasing thallium content.

Below 25,000 with decreasing pressure is the region of maximum complexity. At first, in a pressure interval of one or two thousand kg/cm$^2$, there is a major increase of resistance corresponding to the disappearance of phase II, but the phase which replaces it is not the original phase of the virgin material, but a phase with markedly lower resistance. The creep phenomena are complex and change with composition. At 23 or 24,000 kg/cm$^2$ resistance continues to creep upward after the transition for all three compositions. This creep reverses in direction and becomes a creep downward at 22 or 23,000 for the 10 and 20 per cent

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compositions, but continues as a creep upward for the 30 per cent composition. At a pressure in the neighborhood of 16,000 for all three compositions creep ceases entirely and the system behaves like one in internal equilibrium. Further decrease of pressure results in renewed upward creep extending to the neighborhood of 5,000. The magnitude of this creep increases with increasing thallium content, and for the 30 per cent composition is so rapid between 7,000 and 5,000 as to suggest a discontinuity and a pressure transition in the irreversibly formed compound, if compound it be. Below 5,000 for all three compositions the direction of creep reverses again. This creep was investigated in detail at atmospheric pressure for the 10 and 30 compositions. The creep of the 10 per cent composition was 1.4 per cent in 15 hours and that of the 30 composition 0.5 per cent in 70 minutes. In all cases the final resistance was less than the initial resistance, so that this creep carries the system further away from the initial condition instead of restoring it, as it might be expected it would, and as actually occurs in the bismuth – tin system.

Figures 5 and 6 show the resistance of the 10 and 30 compositions as a function of pressure. Arrows indicate the direction of creep in the several domains. It seems highly probable that the new compound, or whatever it is, has two transitions instead of one; these may perhaps be analogous to the bismuth transitions.

Consider next the resistance of compositions up to 30 per cent thallium in the pressure range above 30,000 up to 100,000. No new transitions appear in this range and the curves are smooth. Furthermore, the curves are surprisingly alike, the ratio of resistance at 30,000 to resistance at 100,000 being constant at 1.28 within experimental error for all compositions from 2 to 30 per cent thallium. This means that the pressure coefficient of resistance of the III phase of bismuth is practically the same as that of the mixtures in varying proportions of III, new irreversible compound, and Hansen's delta.

Next consider the resistances of compositions 40, 50, 80 and 90 per cent Tl. In the range up to 30,000 resistance is a smooth single valued function of pressure with no creep, and in the range 30,000 to 100,000 smooth and without creep (the experimental set-up does not permit an answer to the question as to whether

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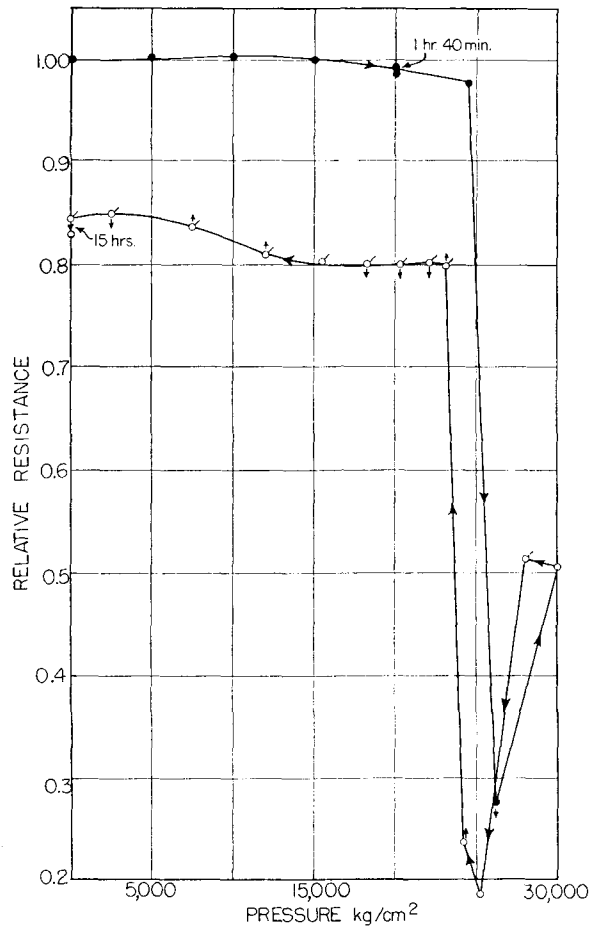


Figure 5. Relative resistance at room temperature of the alloy Bi 90 – Tl 10 as a function of pressure. The arrows attached to some of the points indicate the direction of drift of resistance at constant pressure and temperature.

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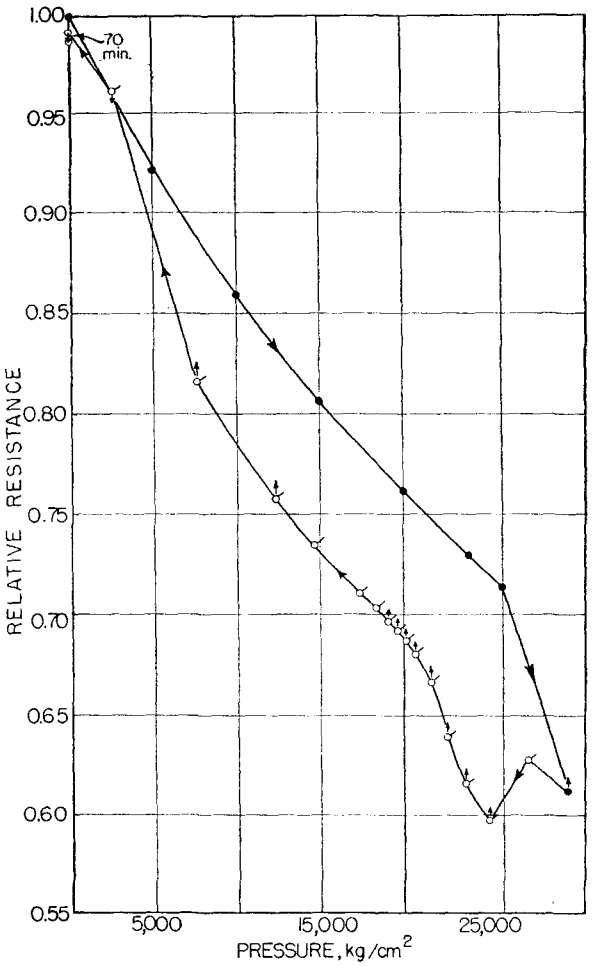


Figure 6. Relative resistance at room temperature of the alloy Bi 70 – Tl 30 as a function of pressure. The arrows attached to some of the points indicate the direction of drift of resistance at constant pressure and temperature.

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it is single valued in this range). The decrease of resistance brought about by pressure is largest for 40 Tl (presumably Hansen's delta phase), somewhat less for 50 Tl (a mixture of delta and gamma), and notably less and nearly the same for 80 and 90 Tl (presumably Hansen's delta phase).

The thallium transition does not appear until the composition 95 Tl – 5 Bi is reached. At this composition the transition does not appear at all in the pressure range to 30,000, the resistance being smooth and single valued, but it does appear in the run to 100,000 as a marked offsetting of the curve centering around 50,000 and extending over a pressure range of 10,000 kg/cm$^2$. The transition is shown in the table as taking place at 50,000, but this does not mean that 50,000 is the pressure of equilibrium or that the transition under ideal conditions would begin at 45,000. It must be remembered that the method used to 100,000 does not permit readings with decreasing pressure, and that there is always more rounding of the corners than when pressure is truly hydrostatic as in the method used to 30,000.

At higher thallium concentrations the thallium transition shows itself in the 30,000 apparatus, first appearing at 98 Tl – 2 Bi. At this composition there is a slightly accelerated drop of resistance at 25,000 and 30,000, resulting in a relative resistance at 30,000 of 0.741, whereas the resistance would have been 0.754 if the smooth trend up to 20,000 had continued. On release of pressure, the diminution of resistance persists over the entire range and the zero resistance is permanently depressed by 0.4 per cent. The next three compositions, 1.75, 1.50 and 1.25, show accelerated drop of resistance beginning in the general neighborhood of 20,000. The drop at 30,000 with respect to a smooth extrapolation increases from 1.75 to 1.50, but at 1.25 has become less again. At 1.5 per cent the relative resistance at 30,000 (resistance at atmospheric pressure being taken as unity) is 0.611 against 0.742 extrapolated from the curve up to 20,000. On release of pressure marked recovery of resistance occurs, mostly confined to the pressure domain above 15,000. Recovery is not complete, however, and the final zero is depressed by 1.95, 2.13, and 0.32 per cent for the three compositions respectively. At no pressure for these compositions was there noticeable creep. Only the readings with increasing pressure are shown in Table V.

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With the next composition, 1.0 per cent Bi, the character of the phenomena changes. A large drop of resistance occurs between 25,000 and 30,000. On release of pressure an abrupt rise occurs between 25,000 and 20,000, beyond which the curve with increasing pressure is retraced, so that resistance is single valued below 20,000 and there is no permanent change of zero. This behavior was checked by repetition with a second specimen. At the next composition, 0.5 per cent Bi, the transition has entirely disappeared in the range to 30,000, and the resistance is smooth, single valued, and without creep.

In the pressure range above 30,000 the transition of the 0.5 Bi composition, which did not appear at all below 30,000, was found at a pressure somewhat below 45,000. The other dilute compositions also showed an enhanced transition, the beginnings only of which were found in the 30,000 apparatus. The pressures at which the accelerated decrease of resistance marking the beginning of the transition began to be perceptible were 42,750, 41,000, 43,600, 33,900, and 41,900 respectively for the compositions 2.0, 1.75, 1.5, 1.0 and 0.5 per cent Bi. This progression of values is at least not inconsistent with a progressive decrease of the pressure of the transition coupled with an increasing sluggishness which retards the appearance of the transition.

In view of these two opposed tendencies it became a problem as to how best to present the data. It is obvious that the results with the 30,000 apparatus are valueless as indications of the total discontinuity of resistance for the 2.0, 1.75, 1.5 and 1.25 compositions. On the other hand, the measurements with the 100,000 apparatus do not give acceptable values for the pressure of initiation of the transition, this pressure always being too high with this apparatus. In tabulating the results one method was adopted for the range of great sluggishness and another for the more sprightly transitions. For compositions 2.0, 1.75 and 1.5 the magnitude of the discontinuity at the transition was taken from the 100,000 measurements, the mean pressure of the transition taken as 50,000, and connection made with the 30,000 measurements by adjusting the relative resistances of the two runs at 20,000 to equality. This does not mean at all that the mean pressure of the transition is 50,000 for all these compositions, but it does mean that the combined effect of increasing depression of

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the pressure of transition and increasing sluggishness was such that the transition was complete for all these compositions at pressures not far from 50,000 and always below 60,000. The conclusion as to the completion of the transition was drawn from the general character of the curves between 50,000 and 100,000. The 5 per cent Bi composition is handled in the table by the same method, the discontinuity of resistance showing up in the 100,000 apparatus, although there was no trace of it to 30,000. The explanation again is sluggishness. For the composition 1 per cent Bi, which gave a comparatively sharp and apparently complete transition in the 30,000 apparatus, all tabulated resistances to 30,000 were taken from measurements with the 30,000 apparatus, and the resistances to 100,000 were adjusted to agreement at 30,000. For the 0.5 per cent Bi composition the transition parameters had to be taken from the measurements to 100,000, adjusting the scale to agreement with the measurements with the 30,000 apparatus at 30,000.

The magnitude of the discontinuity of resistance at the transition shows considerable irregularity, but on the whole tends to become greater as pure thallium is approached and at 5 per cent Bi is markedly smaller.

Consider next the volume compressions in the range to 40,000 kg/cm$^2$. In the composition range up to 30 per cent thallium the phenomena are dominated by the bismuth transitions. In none of these measurements of compression was there any perceptible difference between curves with increasing and decreasing pressure, nor was there any permanent change of volume. This means that the compound, if such it is, formed irreversibly at pressures above 20,000, has practically the same volume as the low pressure modification of bismuth, and that the volume changes associated with the pressure transition or transitions of the compound are too small to detect. The discontinuities of volume at the two bismuth transitions shown in Table V become less with increasing thallium content. The relation is approximately linear in composition. Extrapolation gives a vanishing volume change at 34 per cent Tl, both for the transition from I to II, and for the over-all transition from I to III. We may take it, therefore, that 34 per cent Tl marks the beginning of the domain of Hansen's delta phase. The mean pressure of the two bismuth transitions

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is not appreciably displaced with changing thallium content. The I – II transition tends to become more sluggish, but the II – III transition remains sharp over the entire range. It suggests itself that thallium does not form solutions with either phase II or phase III of bismuth.

The compressions of the next three compositions, 40, 50 and 80 per cent thallium, are nearly the same, which means that the compressibility of the delta and gamma phases of Hansen is approximately the same. Furthermore, it is to be noticed that the compressions of pure bismuth and pure thallium are nearly the same in the pressure range below the transitions; this is also the compression of the delta and the gamma phases.

The compressions of the dilute solutions of bismuth in thallium from 2 per cent Bi on, show the phenomena of the thallium transition in a much more clean cut way than did the resistance phenomena. The width of the hysteresis zone between the transition with increasing and decreasing pressure is here so narrow that a mean pressure can be established for the transition as a function of pressure with some precision and is shown in the table. The pressure of the transition is a linear function of the bismuth content and extrapolates to 36,000 kg/cm$^2$ for pure thallium. This is sufficiently close to the 40,000 for pure thallium, and leaves no room for doubt but that the transition found here is between phases II and III of thallium (that is, it is the high pressure transition), and that the transition to thallium I, the high temperature modification, is in no wise involved, although Hansen's diagram suggests the possibility. Extrapolation in the other direction gives zero pressure for the transition at 3 per cent bismuth. This would mean that at 5 per cent bismuth the phase normally present at atmospheric pressure is phase III, whereas the resistance measurements gave a transition for this composition in the 100,000 apparatus. Two possible reasons suggest themselves for the much greater sluggishness of the resistances as compared with the volumes. In the first place, the volume measurements involve a slight component of shearing stress, whereas the resistances up to 30,000 were determined under truly hydrostatic conditions. It has been found in other cases that shearing stress may be very effective in eliminating sluggishness. In the second place, the shapes and dimensions of the specimens

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are different. For the resistance measurements the specimens were in the form of a slender wire, so that the transition would have to propagate itself over a long path to be complete. The specimen of the compression measurements was in the form of a compact slug 6 mm in diameter and 3 mm thick, so that the transition, once initiated, could spread to all parts with only a short distance of propagation.

The changes of volume at the transition are nearly constant as a function of composition from pure thallium to 1.5 per cent Bi. Here there is an abrupt downturn, dropping off to one half at 2 per cent bismuth.

Shearing runs were made on the following compositions as well as the pure metals: 100, 90, 80, 70, 60, 50, 20, 1 and 0 per cent Bi. The pressures were pushed to 100,000 kg/cm$^2$ for all compositions except pure thallium. The shearing curves show a regular progression in character. Pure bismuth has a pronounced maximum and minimum in the neighborhood of 30,000 and a second maximum and minimum near 65,000. These mark known transitions. At 90 per cent Bi the lower maximum and minimum remains, although less pronounced, but the upper maximum and minimum has straightened out into a point of inflection. At 80 Bi the lower maximum and minimum flatten out further to a nearly horizontal stretch and a new flat place appears near 70,000. At 70 Bi the lower maximum and minimum have entirely disappeared, but a new maximum has appeared at 50,000 and minimum at 70,000. At 60 Bi the new episode is much sharpened, the maximum now being at 35,000 followed by an unusually steep descent to the minimum at 65,000. At 50 Bi this episode is flattened out to a nearly horizontal stretch reaching from 30,000 to 80,000. At 20 Bi the curve has straightened to approximately a line over its entire length, with a small point of inflection in the lower half and a slight upward hook at the very top. At 1 per cent Bi the curve is nearly straight with a shallow point of inflection near 40,000. At 100 Tl the curve is again nearly straight, but the point of inflection at 40,000, marking the known transition of pure thallium, is accentuated. The absolute shearing strengths of the nine compositions at 100,000 were respectively: 1,210, 1,830, 1,740, 2,570, 840, 1,270, 1,120, 1,520 and 1,430 kg/cm$^2$, the value for pure thallium being extrapolated from 80,000. Notice the unusually low shearing strength,

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840, of the 60 – 40 composition. This is the lowest value hitherto observed for any material at this pressure.

The very marked shearing episode between 35,000 and 65,000 of the 60 – 40 composition is not reflected in either the resistance or the volume phenomena. Again we seem driven to assume that there are transitions characteristic of shearing stress as distinguished from hydrostatic pressure.

## Discussion and Summary

Only limited aspects of the data can be touched here. In fact, the data themselves are regrettably incomplete, in spite of the fact that they are often so numerous as to raise an embarrassing problem as to the best method of presentation. Obviously temperature should be added as an independent variable in order to give an adequate picture. A complete mapping out of the pressure-temperature relations will involve an enormous amount of work. Aspects of the present limited data which must eventually yield to theoretical understanding include, for example, the specific effects of pressure on resistance at different compositions. There is as yet no adequate theory of the effect of pressure on the resistance of metals, and little has been done in this field in the last twenty-five years. It would seem that perhaps we have here sufficient new experimental material to justify a renewed experimental attack on this problem. If such a renewed theoretical attack is made one should at first confine his attention to those systems for which the relation between pressure and resistance is single valued and without hysteresis or creep.

Perhaps the most obvious topic for discussion is the role played by the polymorphic transition of thallium. We have to ask how is the transition modified by the addition of an alloying element? Is the pressure raised or lowered? How is the character of the transition modified? Thermodynamics can give a formal answer to the second question, but this is not in general very helpful, because the answer of thermodynamics is formulated in terms of such concepts as the molecular weight of the dissolved metal, which is a much less clean cut concept for alloys than for such systems as aqueous solutions, for example. Thermodynamics does suggest, however, that depending on the way in which the dis-

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solved metal is distributed between the two phases the transition pressure may be either raised or lowered. In the case of a mechanical mixture, such as occurs in ordinary eutectic systems, the pressure of the transition and the sharpness both ought to be independent of composition, and the volume change at the transition should be proportional to the fractional part of the whole volume occupied by the transitioning member, in this case thallium.

Of the systems of this paper Tl – Cd comes the nearest to being a simple mechanical mixture over the entire range. In Table I the pressure of the transition is shown as increasing with increasing content of cadmium. This may not be real, but may be an effect of subcooling. In any event, even here, the phenomena connected with the initiation of the new phase are not clean cut. The total volume change associated with the transition, on the other hand, behaves approximately as expected.

The system Tl – In is, after Tl – Cd, the simplest of the systems of this paper. The pressure of the thallium transition is lowered by the addition of indium, as shown equally by measurements of resistance or volume. The transition pressure is lowered to atmospheric by the addition of somewhere between 30 and 40 atomic per cent indium. At higher indium concentrations the transition thus fades out of the picture; it might perhaps be picked up again at lower temperatures. There would, however, be difficulties because the sluggishness of the transition increases markedly. From the fact that both corners of the transition are rounded one can draw the conclusion that indium is soluble in both phases of thallium.

The transition phenomena in the other three systems, lead, tin and bismuth, are more complicated. It is known that thallium dissolves considerable quantities of these three metals, but the phase relations in the immediate neighborhood of pure thallium may not be adequately given by the present diagrams of the metallurgist. This is certainly the case for the system Tl – Pb, for which Tang and Pauling found X-ray evidence for the compound $PbTl_7$. This means that in the range from 87.5 to 100 per cent Tl the system consists: first of a homogeneous range with the structure of $PbTl_7$, second a range of mechanical mixture of $PbTl_7$ and the lattice of pure Tl, and finally a homogeneous

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range of the thallium lattice in which $PbTl_7$ is dissolved. The pressure phenomena in connection with the thallium transition must, therefore, be confined to a composition range not much wider than 10 per cent extending from pure thallium down. This suggests in general that a study of the effect of pressure on a transition can be used as a tool in investigating phase diagrams. If a phase ordinarily produced by pressure drops out of the picture at a composition where the ordinary phase diagram gives one a right to expect it, then one may suspect that an unknown new phase has insinuated itself into the situation.

The immediate application of these ideas to the Tl – Pb system is complicated by the probability that the new phase $PbTl_7$ itself has a transition under pressure. It would require much more work on the Tl – Pb system, particularly at small lead concentrations, to straighten out all the relations here. It is probable that a more clean cut application of this idea can be made to the Tl – Sn system. Here the thallium transition drops out of the picture in the neighborhood of 10 per cent Sn, suggesting the existence of a new compound analogous to $PbTl_7$, but this new compound is simpler in that it has no pressure transition, so that beyond 10 per cent Sn there are no transition phenomena in this system. With regard to the Tl – Bi system it would seem fairly certain that the pressure of the thallium transition is depressed by the addition of bismuth. It is probable that the transition drops out altogether in the neighborhood of 5 per cent Bi, and it is not impossible that a new compound analogous to $PbTl_7$ occurs here also, but clean cut interpretation is not possible because of the great sluggishness of the transition, which affects resistance and compression measurements unequally.

I am indebted to Mr. Charles Chase for setting up many of the specimens, and to Mr. L. H. Abbot for preparation of the alloys and many of the measurements.

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# Effects of Pressure on Binary Alloys

## IV

### Six Alloys of Bismuth

By P. W. Bridgman

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## Introduction

In this fourth paper of the series[1] the effects of pressure on six more alloys of bismuth with low melting metals (except silver) are described. This is in addition to the alloys of bismuth with tin, cadmium, and thallium already described in earlier papers of this series. The parameters measured are the same as in the earlier papers, namely: density, specific resistance, temperature coefficient of resistance, change of resistance under pressure in two pieces of apparatus, one to 30,000 and the other to 100,000 kg/cm$^2$, volume compression to 40,000 kg/cm$^2$, and plastic shearing strength, usually to 80,000, but sometimes to 100,000. The technique of preparing the specimens and making the measurements is the same as before.

The phenomena shown by the alloys of bismuth are, in general, by far the most complicated of any alloys investigated hitherto. The complications arise from the three modifications of bismuth and the irreversible formation under pressure of new phases or compounds, which themselves may exhibit polymorphism under pressure. Often the systems are not in a state of complete internal equilibrium, as shown by creep of electrical resistance after al-

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# TABLE I

## Bismuth — Silver

| | 100 Bi | 50 Bi 50 Ag | 100 Ag |
|---|---|---|---|
| Density | 9.81 | 9.93<br>10.16 | 10.49 |
| $\rho_{00} \times 10^6$ | 131 | 69 | 1.62 |
| Temperature Coefficient | .00331 | −.00039 | .0040 |
| Pressure kg/cm² | | Rp/Ro | |
| 0 | 1.000 | 1.000 | 1.000 |
| 5,000 | 1.098 | 1.065 | .983 |
| 10,000 | 1.210 | 1.124 | .966 |
| 15,000 | 1.335 | 1.179 | .951 |
| 20,000 | 1.474 | 1.230 | .936 |
| 25,000 | 1.638 | 1.272 | .923 |
| 30,000 | .900 | .537 | .910 |
| 40,000 | .867 | .522 | .885 |
| 50,000 | .837 | .508 | .864 |
| 60,000 | .811 | .496 | .846 |
| 70,000 | .787 | .484 | .831 |
| 80,000 | .764 | .474 | .819 |
| 90,000 | .747 | .466 | .809 |
| 100,000 | .730 | .459 | .802 |
| | | $-\Delta V/Vo$ | |
| 5,000 | .0163 | .0130 | .0047 |
| 10,000 | .0290 | .0241 | .0094 |
| 15,000 | .0410 | .0342 | .0139 |
| 20,000 | .0520 | .0436 | .0182 |
| 25,000 | | .0525<br>.1173 | .0224 |
| 30,000 | .1526 | .1248 | .0264 |
| 35,000 | .1601 | .1315 | .0302 |
| 40,000 | .1670 | .1377 | .0338 |

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terations of pressure, so that it is possible to obtain only a comparatively rough picture of the effects of pressure in some instances.

## Detailed Presentation of Data

*Bismuth — Silver.* According to Hansen[2] this forms a simple eutectic mixture of silver containing a small percentage of bismuth in solution and practically pure bismuth. The chief interest was in the possible existence of new phases under pressure, and for this purpose only a single composition was studied, of nominally 50 — 50 atomic per cent. Because of the wide range of melting points the casting was more inhomogeneous than usual; the density of the whole casting was 10.065, against densities of 9.926 and 10.160 for approximately the upper and lower halves. The expected density of the mechanical mixture is 10.03.

Mechanically the alloy was too hard to be successfully extruded to wire for the resistance measurements, which were made on plates squeezed at 250°. The resistance measurements were made by the "four razor blade" technique,[3] so that the specific resistance, but not the coefficients, is of inferior accuracy. The mechanical hardness was not sufficiently great to demand the use of an indium sheath in the measurements of compression.

The numerical results are shown in Table I, along with the values for the pure components. Since this alloy consists in large part of pure bismuth it is to be expected that it will show the regular bismuth transitions, albeit diminished in scale. This is indeed the case. The first transition, as shown by the resistance measurements, which are the most sensitive, occurs between 25,000 and 25,700 kg/cm$^2$, essentially the same as for pure bismuth.

On release of pressure from 30,000 the curve obtained with increasing pressure was retraced with an upward displacement of 1.1 per cent. This is less than is often shown by pure bismuth, and is doubtless a result of changes of dimensions and orientation of the grains as a result of the transitions. This effect is disregarded in the table, where the resistance is given as single valued. No new effect occurs beyond 30,000. The drop of resistance between 30,000 and 100,000 is 14.5 per cent, against 18 per cent for pure bismuth and 11 per cent for pure silver.

It is not possible to calculate the various changes by any simple

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rule of mixtures. The specific resistance, $69 \times 10^{-6}$, is much larger than would be calculated by Lichtenecker's rule[4] (one of the most successful rules yet proposed for mechanical mixtures), which gives $27 \times 10^{-6}$. The bismuth component in the alloy is sufficiently dominating to produce an over-all increase of resistance under pressure, like pure bismuth, but the curvature with pressure is in the reverse direction. Furthermore, the reduction in pressure coefficient is by a considerably greater factor than is the reduction in specific resistance. Although the positive increment of resistance under pressure is not as great as would be expected, the fractional drop of resistance on passing through the transitions is greater. The relative resistance immediately after the transitions in terms of that immediately before is 0.55 for pure bismuth and 0.42 for the mixture.

The relations for compression are the opposite of those for resistance, for the volume decrements measuring the normal compressibility of the alloy are greater than to be expected from the additivity of the components, but the volume decrements at the transitions less.

In the case of both resistance and volume the failures of the expected additive relations are not by large amounts and may be ascribed at least in part to failures of isotropy in the bismuth grains, although it is difficult to believe that the entire effect is due to this.

The measurements of plastic flow strength were made to only 80,000 kg/cm$^2$. The curve showed a single well-marked episode at the I – II – III transition; above that it rises with normal downward curvature to a shearing strength of 2,500 kg/cm$^2$ at a pressure of 80,000 kg/cm$^2$.

*Bismuth – Zinc.* According to Hansen[5] the system consists at room temperature of a mechanical mixture of practically pure zinc with bismuth containing a few per cent of dissolved zinc. The primary interest is whether there is a new high pressure phase, and for this purpose only a single composition, 50 – 50 atomic per cent, was investigated.

This alloy probably represents the extreme of inhomogeneity among those of this investigation; this might be expected from the phase diagram which shows two immiscible liquid phases. Densities of pieces of the casting were obtained ranging from

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# TABLE II

## Bismuth – Zinc

| | 100 Bi | 50 Bi<br>50 Zn | 100 Zn |
|---|---|---|---|
| Density | 9.81 | 8.65<br>9.30 | 7.08 |
| $\rho_{00} \times 10^6$ | 131 | 43 | 5.5 |
| Temperature Coefficient | .00331 | .00227 | .00408 |
| Pressure kg/cm² | | $R_p/R_o$ | |
| 0 | 1.000 | 1.000 | 1.000 |
| 5,000 | 1.098 | 1.022 | |
| 10,000 | 1.210 | 1.038 | .937 |
| 15,000 | 1.335 | 1.053 | |
| 20,000 | 1.474 | 1.064 | .887 |
| 25,000 | 1.638 | 1.073 | |
| 30,000 | .900 | .519 | .847 |
| 40,000 | .867 | .500 | .812 |
| 50,000 | .837 | .482 | .783 |
| 60,000 | .811 | .468 | .756 |
| 70,000 | .787 | .457 | .733 |
| 80,000 | .764 | .446 | .713 |
| 90,000 | .747 | .438 | .695 |
| 100,000 | .730 | .430 | .679 |
| | | $-\Delta V/V_o$ | |
| 5,000 | .0163 | .0121 | .0079 |
| 10,000 | .0290 | .0229 | .0157 |
| 15,000 | .0410 | .0328 | .0229 |
| 20,000 | .0520 | .0417 | .0297 |
| 25,000 | | .0505 | .0362 |
| 30,000 | .1526 | .1039 | .0424 |
| 35,000 | .1601 | .1105 | .0484 |
| 40,000 | .1670 | .1160 | .0541 |

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8.65 to 9.30, against 8.97 to be expected for the homogeneous mechanical mixture.

The resistance specimen for 30,000 was extruded to wire at 200°. The numerical results are shown in Table II. As is to be expected, the bismuth transition is cleanly shown, but with diminished discontinuities. The pressure at which the discontinuities occur is unaffected by the zinc.

The specific resistance at atmospheric pressure agrees surprisingly well with that given by Lichtenecker's rule, the actual value being $43.2 \times 10^{-6}$ against 42.4 calculated. However, at 100,000 the agreement is not nearly as good, the actual specific resistance being $18.6 \times 10^{-6}$ against 28.2 calculated. A rearrangement of the geometrical involvement of the two components at the phase change suggests itself. At pressures below the transitions resistance increases with pressure, the bismuth dominating the situation to at least this extent, but the increase is comparatively small, and the curvature is downward, instead of up as for bismuth. At the transition, resistance drops by a factor 0.49, against the factor 0.55 for pure bismuth. The bismuth being diluted to approximately one half by the zinc, one would expect a factor considerably larger than 0.55, instead of a lower factor. Mutual solubility of zinc and high pressure bismuth is therefore to be recognized as a possibility.

On release of pressure from 30,000 the curve with increasing pressure was retraced with unusual closeness, there being an upward displacement of only 0.2 per cent. This is probably of no significance and the resistance is given in the table as single valued. There is no new episode between 30,000 and 100,000. The decrease of resistance from 30,000 to 100,000 is 17 per cent for the mixture, against 18 per cent for pure bismuth and 20 per cent for pure zinc.

The volume relations at the transition are not far from those to be expected by a simple additivity relation from the pure components.

The shearing curve shows only a single episode at the known bismuth transition, beyond which it rises with only slight curvature in the normal downward direction to 2,300 kg/cm$^2$ at 80,000 kg/cm$^2$.

*Bismuth – Tellurium.* This was examined in only two dilute mixtures of tellurium with bismuth, 0.25 and 1.0 atomic per cent

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tellurium. The chief interest of the investigation was to find whether there is any evidence for solubility of tellurium in bismuth. Hansen[7] states that the solubility of tellurium in bismuth is very slight at room temperature, but leaves open the question as to whether it is detectible. At higher concentrations Hansen gives a compound $Bi_2Te_3$ which dissolves both bismuth and tellurium, with a domain of mechanical mixture on both sides of the compound.

The tellurium used in this investigation had been used in previous measurements of the effect of pressure[6] which I owe to the courtesy of Professor Harry Hall. It had been highly purified to an impurity content of the order of $10^{-7}$.

The densities of the two compositions were found to be less than that of pure bismuth, and do not suggest, within the accuracy of the measurements, the existence of solubility.

The resistance specimens for 30,000 were made by extrusion; the 0.25 composition was extruded at 150°, and the 1.00 composition with difficulty at 230°, extrusion of the latter composition not having been successful at either 150° or 200°. The specific resistance of the two compositions departs irregularly from that of pure bismuth, the first being low and the second high. The departure is not large and perhaps within the limits of the possible effect of non-isotropy. In any event, the resistance gives no evidence of any solubility of tellurium in bismuth, the expected effect of which would have been an initial increase of specific resistance. The evidence afforded by the temperature coefficient is the same; the coefficient of the 0.25 composition remains high, whereas a drop would be expected if there were solubility.

The effect of pressure on resistance is shown in Table III. There was no creep at any pressure except in the immediate neighborhood of the transitions, where the creep was in the direction to be expected from the running of the transitions. The two transitions run cleanly with no displacement of pressure as compared with pure bismuth. The magnitude of the discontinuities is somewhat greater than for pure bismuth, but the effect of pressure on resistance in the continuous range below the transition somewhat less. There is a parallelism between these comparatively small effects and the deviations of specific resistance from that of pure bismuth. Whether there is any significance in

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# TABLE III

## Bismuth — Tellurium

| | 100 Bi | 99.75 Bi 0.25 Te | | 99.00 Bi 1.00 Te | |
|---|---|---|---|---|---|
| Density | 9.81 | 9.78 | | 9.76 | |
| $\rho_{00} \times 10^6$ | 131 | 96 | | 117 | |
| Temperature Coefficient | .00331 | .00483 | | .00401 | |
| Pressure kg/cm² | | Rp/Ro | | | |
| 0 | 1.000 | 1.000 | .909 | 1.000 | .887 |
| 5,000 | 1.098 | 1.069 | .969 | 1.081 | .963 |
| 10,000 | 1.210 | 1.142 | 1.035 | 1.165 | 1.020 |
| 15,000 | 1.335 | 1.223 | 1.110 | 1.252 | 1.085 |
| 20,000 | 1.474 | 1.312 | 1.188 | 1.344 | 1.150 |
| 25,000 | 1.638 | 1.412 | | 1.438 | |
| 27,000 | | .242<br>.238<br>.638 | | .201<br>.196<br>.525 | |
| 30,000 | .900 | .628 | | .517 | |
| 40,000 | .867 | | | .493 | |
| 50,000 | .837 | | | .472 | |
| 60,000 | .811 | | | .453 | |
| 70,000 | .787 | | | .437 | |
| 80,000 | .764 | | | .425 | |
| 90,000 | .747 | | | .415 | |
| 100,000 | .730 | | | .407 | |
| | | $-\Delta V/Vo$ | | | |
| 5,000 | .0163 | .0146 | | .0143 | |
| 10,000 | .0290 | .0279 | | .0270 | |
| 15,000 | .0410 | .0398 | | .0388 | |
| 20,000 | .0520 | .0509 | | .0501 | |
| 25,000 | | .0616 | | .0611 | |
| | | (a) | | (b) | |
| 30,000 | .1526 | .1535 | | .1520 | |
| 35,000 | .1601 | .1608 | | .1595 | |
| 40,000 | .1670 | .1670 | | .1660 | |

(a) At 26,500, $\Delta V_{I\text{-}II} = .0476$, $\Delta V_{II\text{-}III} = .0353$

(b) At 26,500, $\Delta V_{I\text{-}II} = .0477$, $\Delta V_{II\text{-}III} = .0341$

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these variations or whether they can all be explained by non-isotropy and inhomogeneities would require much further experimenting to decide.

A special study was made of the sharpness of the transitions, since this gives presumptive evidence as to solubility. It is to be expected that the corners of the transition will be rounded if there is appreciable solubility. With the 0.25 composition and with decreasing pressure the III – II transition started and ran abruptly in a pressure range 160 kg/cm² wide, and the II – I transition similarly in a zone 150 kg/cm² wide. The 1.0 composition gave, with increasing pressure, a perceptible starting of the I – II transition for a pressure increment of 40 kg/cm², at 25,300, the value for pure bismuth. Perceptible creep due to this transition continued to 25,900. The II – III transition started perceptibly at 27,300, and was still running perceptibly at 27,500. On the whole, the delay in starting and the rounding of the corners does not seem to be noticeably different from that of pure bismuth.

On release of pressure, below the transitions, the resistance curve obtained with increasing pressure is not retraced, but lies lower in both cases. This is not the usual direction of change shown by pure bismuth and associated with change of dimensions and orientation, although it is possible that this may be the explanation. The changes of resistance with decreasing pressure are therefore reproduced in the table for what they are worth. It cannot be entirely ruled out that at higher concentrations of tellurium irreversibilities would appear such as have been found for other bismuth alloys, although this does not seem probable.

Resistance measurements were extended from 30,000 to 100,000 only for the 1.0 composition. The results were used without attempting to correct them to secure agreement with the results up to 30,000; the internal evidence is that the uncorrected agreement is unusually good. It will be seen that the proportional resistance to 100,000 of the 1.0 specimen is materially less than for pure bismuth, but the ratio of resistance at 100,000 to that at 30,000 is the same within experimental error, being 0.79 against 0.82.

The compressions are also shown in Table III. The discontinuities of volume at the two bismuth transitions were cleanly resolved, and within experimental error there would seem to be no significant difference in any aspect of the compression of

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either of the two compositions as compared with pure bismuth.

The shearing curves of both compositions show at low pressures the maximum and minimum characteristic of pure bismuth. At the higher pressures there are differences; the curve for composition 0.25 has, at 80,000, turned over to a horizontal tangent, and on release of pressure exhibits a small maximum at 70,000. This reflects the maximum and minimum of pure bismuth in the same vicinity due to the high pressure transition of bismuth. The 1.00 composition, on the other hand, continues to rise nearly linearly to 80,000, and on release exhibits negligible hysteresis. Again the shearing tool proves a more sensitive means of exploration than resistance. The absolute values of shearing strength at 80,000 for pure bismuth, and the 0.25 and 1.0 compositions are respectively: 850, 1,100, and 2,000 kg/cm$^2$. The mechanical stiffening for a small addition of tellurium is thus considerable.

*Bismuth — Antimony*. Hansen[8] gives this system as showing complete miscibility in the solid, the only example known of two completely miscible metals crystallizing in other than the cubic system. Hansen's liquidus curve runs smoothly between the two melting points with the usual shape, and is easy to determine experimentally. The solidus, on the other hand, is difficult to determine experimentally because of seasoning and diffusion phenomena, and there is not satisfactory agreement about it. The best evidence seems to be, according to Hansen, that it runs horizontally at constant temperature all the way from pure bismuth to 75 atomic per cent antimony, where it turns abruptly and rises nearly linearly to the melting point of pure antimony. It might be feared, therefore, that the difficulty of getting homogeneous castings would be greater than usual. As a matter of fact the differences of density between different parts of the same casting were not especially large, rising in the worst case to only 0.06, so that no serious error, as far as density goes, is to be anticipated from inhomogeneity. Twelve compositions were investigated: 1, 2, 3.5, 5, 10, 20, 30, 40, 50, 65, 80, and 90 atomic per cent antimony. The densities are shown as a function of composition in Figure 1. The points lie approximately on a smooth curve, deviating from a straight line in the usual upward direction. The diagram indicates the range of values in those cases where more than one determination was made on the same casting; error from this effect should obviously be small.

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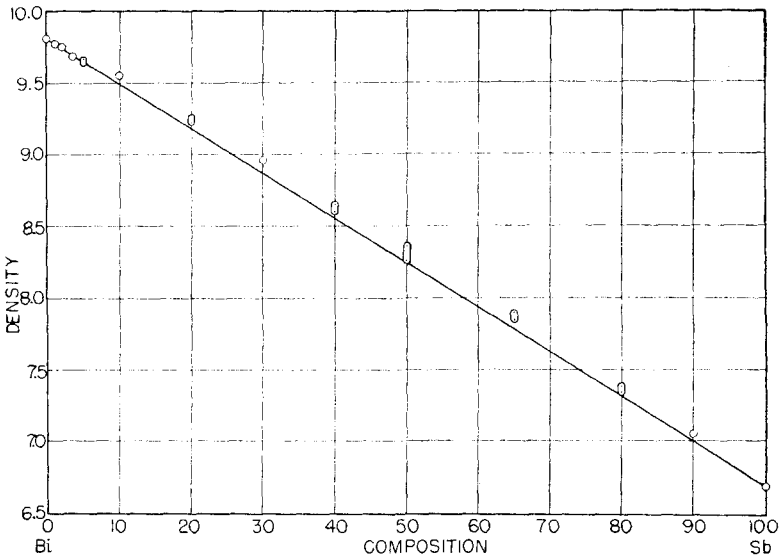


Figure 1. Density of the bismuth – antimony system at atmospheric pressure as a function of composition in atomic per cent.

It might perhaps be anticipated that if the system consists of a continuous series of solid solutions the various pressure phenomena would be especially simple, since there is not much that can happen in such a system. The actual behavior was the exact reverse of this expectation, there being complicated drift and hysteresis effects over the entire range of composition. In fact, none of the resistance measurements presented in the following are measurements corresponding to internal equilibrium, and the table must be taken as only roughly suggesting the general nature of the effects. In this respect the system bismuth – antimony is the least satisfactory of any yet encountered in this program.

The specimens for the resistance measurements to 30,000 were extruded wires when possible. Extrusion becomes increasingly difficult with increasing antimony content, and the last three compositions, 65, 80 and 90 Sb, had to be used in the form of thin plates, squeezed at 250°, 400° and 400° respectively. Later, a wire of composition 35 Bi – 65 Sb was successfully extruded at 270° and used in a determination of the virgin electrical parameters. The other compositions were extruded to wires at the respective

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# TABLE IV

## Bismuth — Antimony

| | | 100 Bi | 99 Bi 1 Sb | | 98 Bi 2 Sb | | 96.5 Bi 3.5 Sb | | 95 Bi 5 Sb | 90 Bi 10 Sb | 80 Bi 20 Sb |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Density | | 9.81 | 9.78 | | 9.76 | | 9.69 | | 9.67 | 9.53 | 9.25 |
| | Before | 131 | 128 | | 137 | | 257, 157 | | 161 | 206 | 228 |
| $\rho_{00} \times 10^6$ | After | 126 | 119 | | 144 | | 171 | | 204 | 225 | 250 |
| | Before | .00331 | .00335 | | .00271 | | −.00114, .00182 | | .00167 | .00092 | .00005 |
| Temperature Coefficient | After | .00326 | .00351 | | .00305 | | +.00124 | | −.00031 | −.00053 | −.00085 |
| Pressure kg/cm² | | | | | | | Rp/Ro | | | | |
| 0 | | 1.000 | 1.000 | 1.000 | 1.000 | .703 | 1.000 | .70 | 1.000 | 1.000 | 1.000 |
| 5,000 | | 1.098 | 1.103 | 1.103 | 1.108 | .785 | 1.120 | .79 | 1.127 | 1.116 | 1.084 |
| 10,000 | | 1.210 | 1.213 | 1.210 | 1.227 | .880 | 1.247 | .89 | 1.271 | 1.251 | 1.175 |
| 15,000 | | 1.335 | 1.330 | 1.351 | 1.334 | 1.00 | 1.378 | 1.01 | 1.435 | 1.397 | 1.274 |
| 20,000 | | 1.474 | 1.443 | 1.506 | 1.38 | 1.12 | 1.48 | 1.14 | 1.600 | 1.533 | 1.360 |
| 25,000 | | 1.638 | 1.564 | 1.680 | 1.22 | 1.253 | 1.50 | 1.26 | 1.768 | 1.653 | 1.426 |
| 30,000 | | .900 | .524 | | .355 | | .301 | | .425 | .380 | .238 |
| 40,000 | | .867 | | | | | | | .406 | .362 | .193 |
| 50,000 | | .837 | | | | | | | .390 | .346 | .162 |
| 60,000 | | .811 | | | | | | | .377 | .333 | .141 |
| 70,000 | | .787 | | | | | | | .366 | .322 | .129 |
| 80,000 | | .764 | | | | | | | .356 | .314 | .122 |
| 90,000 | | .747 | | | | | | | .348 | .306 | .117 |
| 100,000 | | .730 | | | | | | | .340 | .299 | .114 |
| | | | | | | | $-\Delta V/V_0$ | | | | |
| 5,000 | | .0163 | | | | | | | .0140 .0145 | .0139 .0155 | .0129 .0146 |
| 10,000 | | .0290 | | | | | | | .0265 .0281 | .0264 .0283 | .0244 .0276 |
| 15,000 | | .0410 | | | | | | | .0383 .0402 | .0373 .0401 | .0352 .0388 |
| 20,000 | | .0520 | | | | | | | .0496 .0511 | .0476 .0511 | .0455 .0491 |
| 25,000 | | | | | | | | | .0606 {.0617 .1425} | .0590 {.0613 .1374} | .0554 .0814 |
| 30,000 | | .1526 | | | | | | | .1093 .1520 | .0863 .1472 | .0664 .1160 |
| 35,000 | | .1601 | | | | | | | .1590 .1598 | .1332 .1557 | .1037 .1237 |
| 40,000 | | .1670 | | | | | | | .1648 .1659 | .1605 .1635 | .1288 .1305 |

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## TABLE IV – *Continued*

### Bismuth – Antimony

| | | 70 Bi 30 Sb | 60 Bi 40 Sb | 50 Bi 50 Sb | 35 Bi 65 Sb | 20 Bi 80 Sb | 10 Bi 90 Sb | 100 Sb |
|---|---|---|---|---|---|---|---|---|
| Density | | 8.96 | 8.65 | 8.36 | 7.88 | 7.39 | 7.04 | 6.68 |
| $\rho_{00} \times 10^6$ | Before | 283 | 269 | 246 | 210 | | 89 | 33.8 |
| | After | 202 | 190 | 213 | 157 | 101 | 117 | |
| Temperature Coefficient | Before | −.00073 | −.00009 | .00054 | .00130 | | .00284 | .00510 |
| | After | +.00090 | +.00115 | .00093 | .00116 | .00288 | .00285 | |
| Pressure kg/cm² | | | | | $R_p/R_o$ | | | |
| 0 | | 1.000 1.052 | 1.000 1.053 | 1.000 1.013 | 1.000 1.031 | 1.000 1.054 | 1.000 1.211 | 1.000 |
| 5,000 | | 1.041 1.090 | 1.043 1.081 | 1.013 1.032 | 1.028 1.053 | .995 1.045 | 1.001 1.206 | |
| 10,000 | | 1.099 1.139 | 1.087 1.120 | 1.038 1.057 | 1.036 1.055 | 1.005 1.052 | 1.005 1.221 | 1.060 |
| 15,000 | | 1.162 1.195 | 1.136 1.159 | 1.068 1.085 | 1.036 1.045 | 1.025 1.065 | 1.112 1.245 | |
| 20,000 | | 1.224 1.245 | 1.184 1.197 | 1.100 1.113 | 1.033 1.037 | 1.055 1.082 | 1.178 1.268 | 1.104 |
| 25,000 | | 1.275 1.285 | 1.231 1.235 | 1.127 1.134 | 1.027 1.027 | 1.086 1.098 | 1.238 1.284 | |
| 30,000 | | 1.311 | 1.262 | 1.145 | 1.013 | 1.109 | 1.288 | 1.103 |
| 40,000 | | 1.025 | 1.026 | 1.006 | .982 | 1.109 | 1.287 | 1.078 |
| 50,000 | | .635 | .694 | .832 | .824 | 1.052 | 1.246 | 1.021 |
| 60,000 | | .487 | .549 | .665 | .715 | .936 | 1.170 | .938 |
| 70,000 | | .430 | .472 | .525 | .631 | .788 | 1.070 | .837 |
| 80,000 | | .400 | .420 | .425 | .557 | .642 | .954 | .756 |
| 90,000 | | .373 | .381 | .366 | .489 | .515 | .848 | .674 |
| 100,000 | | .349 | .349 | .328 | .426 | .460 | .757 | .605 |
| | | | | | $-\Delta V/V_o$ | | | |
| 5,000 | | .0125 .0148 | .0120 .0141 | .0103 .0142 | .0122 | .0126 | .0137 | .0125 |
| 10,000 | | .0242 .0276 | .0231 .0264 | .0201 .0263 | .0218 | .0237 | .0258 | .0241 |
| 15,000 | | .0350 .0395 | .0330 .0376 | .0290 .0383 | .0319 | .0336 | .0369 | .0349 |
| 20,000 | | .0453 .0506 | .0426 .0497 | .0382 .0480 | .0418 | .0428 | .0472 | .0446 |
| 25,000 | | .0553 .0834 | .0519 .0743 | .0476 {.0579 .0664 | .0513 | .0516 | .0564 | .0538 |
| 30,000 | | .0649 .1089 | .0606 .0894 | .0566 .0757 | .0604 | .0599 | .0650 | .0624 |
| 35,000 | | .0942 .1179 | .0762 .0976 | .0644 .0846 | .0697 | .0678 | .0726 | |
| 40,000 | | .1200 .1268 | .1010 .1051 | .0868 .0930 | .0784 | .0752 | .0798 | |

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temperatures: 250°, 250°, 250°, 250°, 250°, 250°, 300°, 300° and 300° plus, in order of increasing antimony content. Some of these wires were excessively brittle. In spite of the brittleness, however, there appeared to be no cracks or other similar imperfections as shown by the regularity of the readings on first increasing pressure. Open fissures would be likely to give jerky readings. The wires were used after extruding into the air of the room, with no further annealing than that incident to the spontaneous cooling from the mouth of the die. Nearly all compositions show permanent alterations of resistance after exposure to pressure, accompanied by alterations in the temperature coefficient. The latter was determined in the regular way by a temperature cycle from room temperature to 0° back to room temperature. Recovery of zero after the temperature cycle was usually not perfect, or as close as for most other alloys, but the displacements were in all cases small and of a smaller order of magnitude than the permanent displacements by pressure.

The specific resistances and temperature coefficients at atmospheric pressure are shown in Table IV and Figure 2, before and after exposure to pressure. The parameters before the application of pressure show a certain simplicity, and are what might be expected in general of a continuous series of solutions. Specific resistance rises smoothly on the whole with increasing antimony content to a maximum at 30 per cent Sb, from which it diminishes to pure antimony with a minor interruption between 80 and 90 Sb. The temperature coefficient diminishes from the values for the pure metals at either end of the range, reaching a minimum and negative value at the same composition as the maximum of resistance. All this is canonical enough. The parameters after exposure to pressure have more complicated behavior. Specific resistance rises to an absolute maximum at 20 per cent Sb, not at 30 as did the resistance before pressure. From 20 per cent, resistance falls to the value for pure antimony, but with two secondary maxima, one at 50 and the other at 90 Sb. The curve of temperature coefficient shows the usual inverse correlation with specific resistance, the one being high where the other is low and inversely. At the antimony end this affords some credibility to the values for specific resistance. The absolute values of specific resistance for these compositions have greater experimental error

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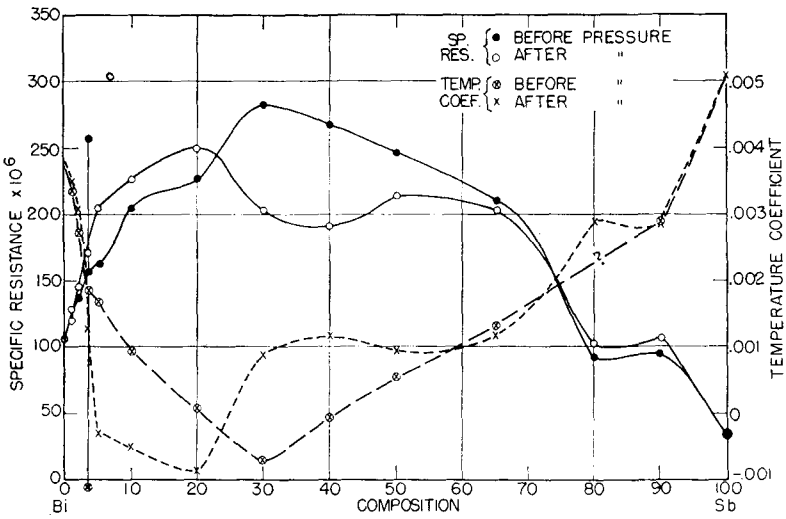


Figure 2. Specific resistance and temperature coefficient of resistance at atmospheric pressure of the system bismuth — antimony, before and after exposure to pressure, as a function of composition in atomic per cent.

than the others. The measurements, which were made on pressed plates instead of wires, suffer from error arising from uncertainty in the dimensions. The temperature coefficients have no such error at any composition. The curves for the parameters "before" and "after" cross. Up to and including 20 per cent Sb the resistance is permanently increased after exposure to pressure (except for an uncertain small effect at 1 per cent Sb); from 20 to 65 per cent Sb the resistance curve "after" lies below that "before," with a slight crossing at higher compositions. For the temperature coefficient "after" lies above "before" up to 3.5 per cent Sb, below for 5, 10 and 20 per cent, above at 30, 40 and 50 per cent, below at 65, not determined at 80, and slightly below at 90.

The sequence of electrical parameters shown in Figure 2 is on the whole regular enough to suggest that it gives an essentially correct picture except at one composition 96.5 Bi — 3.5 Sb. For this the initial specific resistance is nearly twice the expected value and the initial temperature coefficient strongly negative. Both these values are very much out of line. The values after

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exposure of this specimen to pressure, however, fell in the expected range. Repetition of the measurements for the virgin material on another specimen gave values for both parameters in the expected range. The two values for the two different specimens are shown in Figure 2. No explanation suggests itself for this strongly aberrant behavior of a single specimen.

Now consider the behavior of resistance under pressure. It was anticipated that the behavior of the dilute solutions would be especially informative since here we have a rare example of a solution in a metal with positive pressure coefficient of another metal also with positive pressure coefficient. The answer to this question must be sought in the effect of low pressures, below 10,000 kg/cm$^2$, for above 10,000 various aberrancies of behavior appear peculiar to this series. In the table the values for the change of resistance at 5,000 indicate the nature of the effect. The initial increase of resistance first becomes progressively higher when antimony is added to bismuth, but reaches a turning point between 5 and 10 per cent Sb. In this range the effect is not large, ranging from a 9.8 per cent increase at 5,000 for pure Bi to a 12.7 per cent increase for 95 per cent Bi. Beyond 5 per cent Sb the initial positive coefficient slowly decreases, until near 80 per cent Sb the resistance is nearly constant with pressure, the effect of 5,000 kg/cm$^2$ being only a one half per cent decrease. At 90 Sb the effect is very slightly positive again, and assumes a larger positive value for pure antimony. The details of the variation at the antimony rich end are probably not of much significance, since antimony is strongly non-isotropic, the sign of the pressure coefficients being different in different directions. The non-isotropy of bismuth is less marked, the coefficient being always positive and varying from $1.04 \times 10^{-5}$ to $2.03 \times 10^{-5}$ with orientation.[9]

Beyond 5,000 kg/cm$^2$ the abnormalities begin. The first three compositions show an unusual distribution of creep and an unusual smearing out of the bismuth transitions. The composition 1 per cent Sb exhibits slight downward creep beginning at 15,000. This apparently does not presage the I – II transition of bismuth, because even at 27,000, beyond the usual appearance of II, the total downward drop of resistance was only about 3 per cent. Between 27,000 and 27,300 the catastrophic drop of resistance character-

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istic of the appearance of II occurred, the drop being by a factor of 8. At 30,000 there was the jump up characteristic of III. On release III persisted at 27,600, and at 26,000 there was a perceptible downward creep, presaging II, but the transition was not observed to run to completion. At 25,500 the catastrophic upward jump characteristic of I occurred, the recovery to the curve with increasing pressure being practically perfect. The behavior of the one per cent solution is thus much like that of pure bismuth, except that the II and III transitions are somewhat more sluggish, with over shooting of the mark. The next decrease of pressure, from 25,000 to 23,500, carried resistance unexpectedly to a value 12 per cent higher than the initial curve. On further release of pressure a smooth curve was followed, concave upward, such that recovery of the initial zero was perfect. During this release of pressure there was downward drift in the range from 22,000 to 12,000. This downward drift is similar to effects in other alloys of bismuth, so that I was prepared to find the irreversible formation of new phases, with perhaps reversible pressure transitions in the new phases. This did not prove to be the case, but the abnormalities were of another sort. With the next composition, 2 per cent Sb, downward drift began on the first application of pressure at 10,000 and continued increasingly, the curve turning over between 20,000 and 25,000 with a maximum. Again at 27,000 transformation to II or III was only partially complete. Increase from 27,000 to 30,000 carried the system directly into III, the preliminary occurrence of II not having been observed. II was picked up with decreasing pressure, however, at 26,000, where a catastrophic drop of resistance to II occurred after resistance had been steady long enough to give a good value for III. Release from 26,000 to 25,500 gave the catastrophic increase associated with I, creep continuing *upward* both at 25,500 and 24,900. Here we have the reverse transition to I occurring at a pressure markedly higher than normal, indicating not so much a rounding of the corners of the transition as a raising of the whole transition pressure by the dissolved antimony. Furthermore, the recovery of resistance was not back to the original curve, but the decreasing curve lay smoothly *below* the increasing curve, and the final zero was depressed 30 per cent. What is more, creep downward was observed at all pressures on the decreasing curve, including the

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final zero, where it would be expected that the creep would be up to carry the newly formed phase back toward the initial phase.

The composition 3.5 per cent Sb carried the same effects further. The initial increasing curve was similar to that for 2 per cent, downward creep beginning at 10,000 and continuing, with down turning of the curve, below 25,000. Beyond 25,000 the transition was smeared out over a wider range, even at 28,400 the transition not being complete. It was presumably complete at 30,000, and was presumably to III, judging by the absolute resistance and the fact that with decreasing pressure a value was obtained at 28,000 as expected for III. On further release a careful search was made for II, but no trace was found. A transition occurred sharply at 26,000, with immediate upturn of resistance. Apparently the modification II is entirely suppressed at compositions of 3.5 per cent Sb or higher. Further release of pressure below 25,000 gave for the 3.5 composition very much the same curve as for the 2 per cent composition, the decreasing curve lying well below the increasing curve, and again with puzzling downward creep. With the next composition, 5 per cent Sb, the nature of the effects changes. Downward creep has entirely disappeared from the initial curve, which rises approximately linearly, with no turning over, to 26,000, there being no creep anticipatory of the transition even here. At 27,600 the drop indicating the transition had occurred and the creep was still downward, indicating an incomplete transition which was running sluggishly. At 28,000 the transition was still incomplete and running sluggishly, but was perhaps complete at 30,000. On release, no sign was found of II, the upward jump occurring between 27,800 and 26,300. The creep at the latter point was upward, as is normal, indicating a not quite complete transition. From here, with further decreasing pressure, the increasing curve was very nearly retraced, the displacement being upward by a few per cent and with no creep phenomena at any point. That is, this composition behaves like a system in complete internal equilibrium at all points and with a single reversible transition smeared out somewhat sluggishly between 26,000 and 30,000.

The behavior of the next two compositions, 10 and 20 per cent Sb, was essentially like that of the 5 per cent composition — a single transition somewhat smeared out, complete internal equi-

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librium at lower pressures, and a curve with decreasing pressure lying a few per cent higher than with increasing pressure. In the table the resistances of the 5, 10 and 20 per cent compositions are shown single valued in pressure. The reason for doing this is that it is probable that the displacement of zero after application of pressure is a secondary effect due to permanent change of orientation and dimensions associated with the transition, and not a change in the intrinsic properties of the material. This effect is almost always encountered in pure bismuth.

The next compositions, 30, 40 and 50 per cent Sb, show an increasing deviation between increasing and decreasing curves. The decreasing curves now lie above the increasing curves, have less curvature, and show the maximum deviation at zero. There is perceptible down creep, carrying the system back toward the initial resistance, only at zero pressure. It is probable that some slow internal change takes place under pressure, perhaps associated in some way with the transition, but too slow to observe except at zero. The transition has entirely dropped out up to 30,000 for these three compositions, and there is no perceptible creep, even at 30,000, suggestive of it.

The next composition, 65 per cent Sb, marks another change. The changes of resistance produced by pressures up to 30,000 become smaller in magnitude, the over-all changes being of the order of only 5 per cent. In this small range there is marked difference between the results with increasing and decreasing pressure. With increasing pressure resistance passes through a maximum increase of 3.6 per cent in the neighborhood of 10,000, and on release a much sharper maximum near 7,500, with 3 per cent permanent change of zero and no creep after the run. With the next two compositions, 80 and 90 per cent Sb, the effects become progressively larger again, and the difference between increasing and decreasing curves much marked, but again without creep.

The best method of reducing the resistances obtained above 30,000 in the 100,000 apparatus so as to secure agreement with the resistances to 30,000 offers a problem. The difficulty is that hysteresis due to the transition occurs in the overlapping region. The simple course was adopted of multiplying all relative resistances above 30,000 by that factor which would make the relative resistance at 30,000 the same as that obtained with the 30,000

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apparatus. A result of this is that the table indicates a discontinuity of slope, of no physical significance, for all resistances at 30,000. With increasing antimony content the transition gets pushed to higher pressures and becomes more smeared out. For the 20 per cent Sb composition the region of smearing extended from 30,000 to 50,000. With increasing antimony content the region of the smeared out transition becomes more nebulous, and eventually becomes indistinguishable from the maximum of resistance, rapid drop, and eventual reversal of curvature associated with pure antimony. A distinguishing feature of the whole antimony rich end of the series is the comparatively large drop of proportional resistance at the upper end of the pressure range, between 70,000 and 100,000. A plot of the relative change of resistance as a function of composition at any of the higher pressures does not yield smooth curves. It strongly suggests itself that a simple unlimited miscibility does not completely represent the behavior, a conclusion also suggested by the specific resistances.

The compressions are shown in Table IV. Because of hysteresis induced by the transitions the compressions at the bismuth rich end of the series are shown for increasing and decreasing pressure. Both increasing and decreasing curves are constructed so as to have zero compression at atmospheric pressure. The experimental accuracy did not allow separation of any true increase of density after exposure to pressure from the frictional effects, and actual determination of the densities after the pressure runs did not disclose any consistent increase (or decrease) of density. This hysteresis of the compressions parallels the hysteresis already found on the resistances, but it becomes perceptible on the compressions at smaller concentrations of antimony than on the resistances. Above the composition 50 – 50 the effect of the transition on volume drops out in the 40,000 range, and the compressions are shown in the table as single valued. This single-valuedness is in part due to the method of calculation, because there was actually a perceptible difference between the curves with increasing and decreasing pressure which was averaged out in the calculation. The reason for making the calculations in this way was that there is another factor making for increasing hysteresis at high antimony concentrations, namely the increasing mechanical hardness of the alloys. This increases the friction on

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the piston and so the difference between increasing and decreasing readings. This effect is also present to a diminishing extent on the bismuth rich side of 50 – 50 and accounts for some of the hysteresis there. The friction ultimately got so large that the measurements on 10 Bi – 90 Sb were made with a different technique, with the use of an indium sheath. This effectively eliminated the friction and at the same time the hysteresis disappeared. We have proof, therefore, that hysteresis of volume disappears at the antimony end. The hysteresis on resistance on the other hand increases to a marked extent at the 90 Sb composition. The mechanism of this hysteresis of resistance must therefore in this case be different from that at the other end of the series. The absolute value of the compression of this composition is higher than pure antimony or the 80 Sb composition, in line also with the behavior of resistance. Again we have evidence that the system is more complicated than a simple solution.

The shearing curves were not determined for the three most dilute solutions of antimony. The curves do not form a regularly progressing series. The first two compositions, 95 and 90 per cent Bi, do not show the maximum and minimum in the neighborhood of 25,000 – 30,000 characteristic of pure bismuth, but only a well marked region of inflection. Neither do they show the maximum and minimum in the neighborhood of 70,000 – 80,000 characteristic of the high pressure transition of bismuth. The maximum and minimum near 25,000 reappears, however, for the compositions 80 through 35 Bi. At 20 Bi it disappears and is replaced by a not prominent inflection at 40,000 – 50,000. This inflection, which is characteristic of pure antimony, is more strongly accentuated at the 10 per cent Bi composition.

The absolute shearing strengths at 80,000 of the eleven compositions, beginning with pure bismuth and ending with pure antimony were respectively: 850, 3,100, 3,900, 2,900, 2,600, 3,000, 3,250, 3,250, 3,800, 4,300 and 3,900 kg/cm$^2$. Again we have deviations from a smooth progression closely parallel to those of resistance, suggesting greater complication than a simple series of solutions.

*Bismuth – Lead.* The effects of pressure on this system are unusually complex. At the bismuth end of the series pressure produces irreversibly a new phase, in this respect the behavior being

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reminiscent of that in the bismuth – tin system,[10] and at the lead end a new phase appears reversibly at sufficiently high pressures. It will probably conduce to clarity to briefly summarize the conclusions as to the state of affairs before presenting the experimental evidence.

At room temperature and atmospheric pressure the state of the virgin system is, according to Hansen, that indicated in Figure 3a. There are three distinct phases or lattices: alpha, like pure bismuth, gamma like pure lead, and beta, a new phase centering around 70 atomic per cent lead. The homogeneous range of

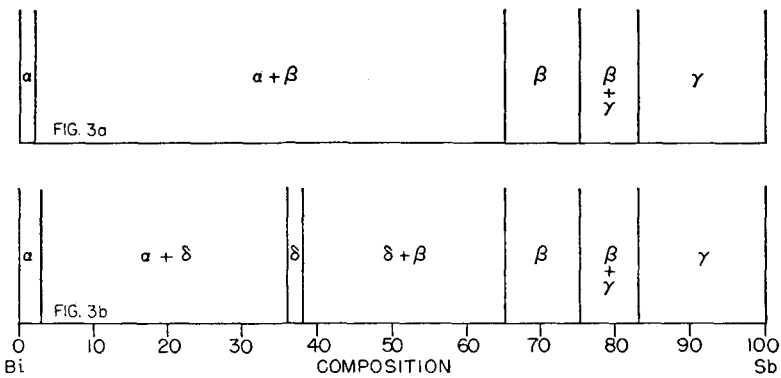


Figure 3. In "a" is shown the constitution, according to Hansen, of the system bismuth – lead at atmospheric pressure as a function of composition in atomic per cent. In "b" the presumptive constitution of the same system is shown after it has been irreversibly changed by exposure to pressure.

alpha is up to only one or two per cent of dissolved beta. The homogeneous range of beta is highly problematical, extending perhaps from 60 to 75 per cent lead. The homogeneous range of gamma is also highly problematical, consisting of a solid solution of beta in gamma, and extending possibly from 100 to 80 per cent lead. The range of mixed alpha and beta is roughly from 1 or 2 to 65 per cent lead, and the range of mixed beta and gamma roughly from 75 to 83 per cent lead. After exposure to pressures of 10,000 kg/cm$^2$ or more, a new phase irreversibly appears on the scene, and the phase diagram at atmospheric pressure becomes as shown in Figure 3b. The new phase, delta, centers around roughly 37 per cent lead, with a narrow range of homogeneity.

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The alpha phase now consists of a solution of delta in pure bismuth, the solubility limits of delta apparently being a little higher than the solubility limits of beta before the irreversible transition. On the low lead side of delta there is a mixture of alpha and delta, and on the high lead side a mixture of delta and beta. The data are not good enough to indicate any difference between the solubility limit of delta in beta as compared with the limit of alpha in beta. Above the homogeneous range of beta all effects of the irreversible appearance of delta disappear. In addition to these irreversible effects, at the lead end from 80 per cent lead on, a new phase appears reversibly at pressures above 30,000, the transition pressure increasing with lead content and running beyond present accessibility above 100,000 at more than 90 per cent lead.

Twenty compositions, in addition to the pure metals, were studied: 0.1, 0.2, 0.5, 1.0, 2.5, 5, 10, 20, 25, 37.5, 45, 50, 60, 69.1, 75, 80, 85, 90, 95, and 97.5 atomic per cent lead.

The castings showed no evidence, by differences of density between different parts, of important or consistent inhomogeneity. The densities, measured before and after exposure to 40,000 kg/cm$^2$, showed no definite pattern of permanent change after exposure to pressure; both densities show irregularities as a function of composition, the densities after exposure being on the whole more regular and therefore presumably more reliable, as would be expected. The densities plotted against composition lie consistently above the straight line joining the end points for the pure metals. The regularity of the points is not sufficient to show the breaks in direction at the boundaries of the homogeneous and mixed ranges that would be expected from the phase relations. From zero to 70 per cent lead the densities lie, with appreciable scatter, on a curve with very slight upward curvature. From 75 to 100 Pb the points lie, with markedly less scatter, on a straight line of smaller slope.

The behavior of electrical resistance will first be described. The resistance effects are larger and more variable than the compression effects, and accordingly more informative. The alloys were all soft and, for the measurements to 30,000, were extruded to wires at temperatures varying from 100° to 120°. The specific resistances should therefore be fairly accurate. At atmospheric pressure the specific resistance of the virgin alloy at first

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increases greatly for small additions of lead, a phenomenon which also occurs in the bismuth – tin system, reaching its maximum, an approximately fivefold increase, for 1 per cent Pb. From here the resistance drops along an approximately smooth catenary curve to the value for pure lead. There are no incidents along this catenary curve sufficiently prominent to justify connecting with the boundaries of the expected homogeneous and mixed regions. It is sometimes conventional to identify the composition of maximum resistance with the limit of solid solubility. If this criterion is accepted, the solubility of the beta phase in alpha would be put as one per cent. However, in this case the curve of resistance against composition departs too much from linearity to lend any particular significance to such a criterion.

The mean temperature coefficient of resistance between 0° and room temperature of the virgin alloy drops abruptly with increasing lead content to negative values, reaching the maximum negative value −0.00318 at 0.2 per cent lead. From the temperature coefficient one might argue with equal plausibility that the solubility limit is 0.2 per cent. Beyond 0.2 per cent the coefficient rises smoothly, but not linearly, and with a point of inflection, to the positive value 0.0042 of pure lead. The temperature coefficient changes sign again in the neighborhood of 10 per cent lead.

Up to but not including 69 per cent lead, all compositions show a permanent change of resistance after exposure to 30,000. This is to be ascribed to the irreversible appearance of the delta phase. The increase of resistance after exposure to pressure is permanent, with no tendency to drift back toward the initial resistance, as was the case for the bismuth – tin system. The new phase irreversibly produced by pressure is therefore possibly absolutely more stable than the virgin phase at atmospheric pressure, as it must be at higher pressure.

The pressure effects will now first be discussed for compositions up to 69 per cent Pb, the limit of the range of the appearance of delta, and in this range the effects produced by 30,000 will be discussed before the effects to 100,000. The net effect of the appearance of the delta phase varies with gross composition. Up to 35 per cent Pb, resistance is permanently decreased after exposure to pressure. The decrease at first rises with increasing lead content, reaching a maximum at 2.5 per cent lead, where the

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specific resistance has dropped from 496 to $325 \times 10^{-6}$, that is, to 0.66 of its initial value. Between 35 and 69 per cent Pb resistance is permanently increased, instead of decreased, by pressure, but by comparatively small amounts. The effects at low concentrations would seem to be a result of the change in the nature of the solute, before pressure the solution being of the beta phase in alpha, and after pressure the delta phase in alpha. This would seem to mean that the intrinsic effect of delta in solution in alpha in raising specific resistance is less than that of beta. After pressure the irreversible transition to delta is apparently complete in the neighborhood of 37 per cent Pb (the chief argument for this will appear later). There is little or no permanent change of resistance at this composition, which must mean that fortuitously the specific resistance of the pure delta phase is approximately the same as that of the equivalent mixture of alpha and beta. In explanation of the reversal of sign of the irreversible change between 37 and 69 per cent Pb, it is to be remarked that the low resistance beta phase, which may be supposed to be the dominant factor in determining the resistance at compositions containing more than 50 per cent of this phase, is much more strongly dominant in the alpha-beta mixtures than in the delta-beta mixtures in this range. A more precise working out of this argument would demand detailed knowledge of the geometrical involvement of the different phases.

The temperature coefficient of resistance as well as specific resistance is in general changed permanently after application of pressure. The numerical values are shown in Table V. In general the temperature coefficient has become numerically less after exposure to pressure, although there are a few minor exceptions. The effect is largest for small concentrations, up to 0.5 per cent Pb.

The discussion so far has been of the permanent changes of resistance after pressure has been applied and released. The curves of resistance as a function of pressure are next to be discussed; it is to be anticipated that the effects will be rather complicated. The smoothed data are shown in Table V; only the most important features can be indicated in the table or described, the total phenomena being too rich and complicated to reproduce in all detail. The data shown in the table are taken from the readings actually made. In many cases drift was perceptibly occurring at

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# TABLE V

## Bismuth — Lead

| | | 100Bi | 99.9 Bi 0.1 Pb | 99.8 Bi 0.2 Pb | 99.5 Bi 0.5 Pb | 99.0 Bi 1.0 Pb | 97.5 Bi 2.5 Pb | 95 Bi 5 Pb |
|---|---|---|---|---|---|---|---|---|
| Density | | 9.81 | 9.81 | 9.81 | 9.81 | 9.84 | 9.87 | 9.89 |
| $\rho_{00} \times 10^8$ | Before | 131 | 294 | 375 | 471 | 533 | 496 | 461 |
| | After | 126 | 247 | 271 | 313 | 291 | 325 | 322 |
| Temperature Coefficient | Before | .00331 | −.00236 | −.00318 | −.00278 | −.00150 | −.00163 | −.00100 |
| | After | .00326 | −.00151 | −.00163 | −.00157 | −.00156 | −.00084 | −.00068 |

| Pressure kg/cm² | | | | | Rp/Ro | | | |
|---|---|---|---|---|---|---|---|---|
| 0 | 1.000 | 1.000 | .865 | 1.000 .740 | 1.000 .702 | 1.000 .540 | 1.000 .604 | 1.000 .693 |
| 5,000 | 1.098 | 1.162 | .957 | 1.158 .813 | 1.135 .754 | 1.053 .594 | 1.005 .619 | .988 .708 |
| 10,000 | 1.210 | 1.353 | 1.033 | 1.310 .869 | 1.240 .785 | 1.066 .610 | .986 .615 | .960 .674 |
| 15,000 | 1.335 | 1.524 | 1.095 | 1.418 .913 | 1.303 .804 | 1.048 .610 | .942 .572 | .909 .596 |
| 20,000 | 1.474 | 1.660 | 1.144 | 1.490 .946 | 1.318 .816 | 1.023 .607 | .902 .522 | .847 .517 |
| 25,000 | 1.638 | 1.730 | 1.177 | 1.510 .959 | 1.310 .823 | 0.95 .610 | .854 .512 | .768 .468 |
| | | .098 | | .078 | .064 | .052 | .054 | .067 |
| 27,000 | | .264 | | .207 | .172 | .135 | .136 | .160 |
| 30,000 | .900 | .259 | | .204 | .1700 | .1330 | .1341 | .1570 |
| 40,000 | .867 | | | | .1622 | .1278 | .1283 | .1500 |
| 50,000 | .837 | | | | .1559 | .1228 | .1232 | .1436 |
| 60,000 | .811 | | | | .1504 | .1185 | .1189 | .1397 |
| 70,000 | .787 | | | | .1460 | .1152 | .1153 | .1357 |
| 80,000 | .764 | | | | .1421 | .1124 | .1124 | .1325 |
| 90,000 | .747 | | | | .1389 | .1099 | .1097 | .1297 |
| 100,000 | .730 | | | | .1358 | .1076 | .1075 | .1274 |
| | | | | | $-\Delta V/Vo$ | | | |
| | | | | | | | | .0149 |
| 5,000 | .0163 | | | | | | .0150 | .0151 .0173 |
| 10,000 | .0290 | | | | | | .0282 | .0281 .0309 |
| 15,000 | .0410 | | | | | | .0409 | .0396 .0437 |
| 20,000 | .0520 | | | | | | .0524 | .0509 .0553 |
| | | | | | | | .0630 | .0619 .0654 |
| 25,000 | | | | | | | .1089 | .1074 .1062 |
| | | | | | | | .1420 | .1405 .1376 |
| 30,000 | .1526 | | | | | | .1505 | .1481 .1463 |
| 35,000 | .1601 | | | | | | .1578 | .1555 .1548 |
| 40,000 | .1670 | | | | | | .1648 | .1618 |

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## TABLE V – *Continued*

### Bismuth – Lead

| | | 90 Bi 10 Pb | 80 Bi 20 Pb | 75 Bi 25 Pb | 62.5 Bi 37.5 Pb | 55 Bi 45 Pb | 50 Bi 50 Pb |
|---|---|---|---|---|---|---|---|
| Density | | 9.97 | 10.18 | 10.25 | 10.56 | 10.72 | 10.77 |
| $\rho_{00} \times 10^6$ | Before | 323 | 188 | 157 | 109 | 86 | 75 |
| | After | 238 | 174 | 150 | 115 | 95 | 80 |
| Temperature Coefficient | Before | −.00005 | +.00065 | +.00083 | .00136 | .00151 | .00147 |
| | After | −.0005 | +.00090 | +.00100 | .00127 | .00127 | .00144 |
| Pressure kg/cm² | | | | Rp/Ro | | | |
| 0 | | 1.000 .648 | 1.000 .923 | 1.000 .983 | 1.000 1.055 | 1.000 1.130 | 1.000 1.071 |
| 5,000 | | .961 .662 | .949 .892 | .944 .943 | .962 .991 | .946 1.065 | .948 1.014 |
| 10,000 | | .916 .623 | .901 .697 | .896 .733 | .905 .68 | .899 .776 | .902 .819 |
| 15,000 | | .850 .538 | .843 .507 | .835 .652 | .824 .622 | .845 .725 | .853 .763 |
| 20,000 | | .768 .393 | .760 .447 | .761 .527 | .737 .591 | .764 .693 | .796 .727 |
| 25,000 | | .649 | .624 | .696 | .614 .568 | .679 .667 | .736 .701 |
| 27,000 | | .120<br>.207 | .244<br>.351 | .286<br>.417 | .551 .559 | | |
| 30,000 | | .204 | .344 | .408 | .548 | .646 | .677 |
| 40,000 | | .196 | .327 | .393 | .527 | .624 | .657 |
| 50,000 | | .188 | .313 | .379 | .508 | .603 | .640 |
| 60,000 | | .182 | .301 | .367 | .492 | .582 | .626 |
| 70,000 | | .177 | .292 | .357 | .479 | .563 | .614 |
| 80,000 | | .173 | .284 | .347 | .467 | .549 | .604 |
| 90,000 | | .169 | .277 | .338 | .448 (a) | .534 (a) | .589 (a) |
| 100,000 | | .166 | .272 | .329 | .417 | .504 | .575 |
| | | | | − ΔV/Vo | | | |
| 5,000 | | .0144 .0152<br>.0187 | .0145 .0169<br>.0218 | .0139 .0151<br>.0215 | .0136 .0159<br>.0427 | .0139 .0145<br>.0346 | .0128 |
| 10,000 | | .0272 .0326 | .0273 .0377 | .0261 .0381 | .0268 .0299<br>.0522<br>.0565 | .0263 .0463 | .0239 |
| 15,000 | | .0390 .0466 | .0388 .0521 | .0374 .0521 | .0368 .0691 | .0390 .0571 | .0340 |
| 20,000 | | .0504 .0597 | .0507 .0653<br>.1039 | .0491 .0640 | .0487<br>.0535 .0804 | .0644 (b) .0670 | .0436<br>.0604 |
| 25,000 | | .0620 .0714<br>.1035<br>.1322 .1285 | .0627<br>.1173 .1157 | .0605 .0742<br>.0946 .0962<br>.1125 .1100 | .0579 .0907<br>.0789<br>.0947 | .0757<br>.0775 .0768 | .0527<br>.0694 |
| 30,000 | | .1410 .1384 | .1272 .1257 | .1208 .1186 | .1044 .1001 | .0865 | .0776 |
| 35,000 | | .1490 .1468 | .1345 .1327 | .1286 .1270 | .1120 .1082 | .0952 | .0855 |
| 40,000 | | .1560 .1545 | .1412 .1385 | .1355 .1346 | .1185 .1152 | .1030 | .0926 |

(a) Cusp in this interval.

(b) At 17,370, .0433 and .0595.

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## TABLE V — *Continued*

### BISMUTH — LEAD

| | | 40 Bi 60 Pb | | 30.86 Bi 69.14 Pb | 25 Bi 75 Pb | | 20 Bi 80 Pb | | 15 Bi 85 Pb | 10 Bi 90 Pb | 5 Bi 95 Pb | 2.5 Bi 97.5 Pb | 100 Pb |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Density | | 11.07 | | 11.21 | 11.21 | | 11.24 | | 11.26 | 11.28 | 11.32 | 11.35 | 11.35 |
| | Before | 72 | | 50 | 46.5 | | 39.3 | | 33.5 | 30.4 | 24.4 | 22.1 | 19.1 |
| $\rho_{00} \times 10^6$ | After | 74 | | 50 | | | | | | | | | |
| Temperature Coefficient | Before | .00147 | | .00164 | .00189 | | .00221 | | .00253 | .00282 | .00338 | .00369 | .00421 |
| | After | .00144 | | | | | | | | | | | |
| Pressure kg/cm² | | | | | | | | | Rp/Ro | | | | |
| 0 | | 1.000 | 1.040 | 1.000 | 1.000 | 1.008 | 1.000 | 1.015 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 |
| 5,000 | | .946 | .986 | .947 | .939 | .958 | .944 | .973 | .945 | .941 | .938 | .936 | |
| 10,000 | | .899 | .817 | .902 | .895 | .916 | .898 | .933 | .892 | .892 | .884 | .881 | .873 |
| 15,000 | | .851 | .763 | .863 | .860 | .878 | .861 | .897 | .854 | .850 | .841 | .833 | |
| 20,000 | | .803 | .726 | .829 | .830 | .842 | .822 | .862 | .818 | .812 | .800 | .793 | .779 |
| 25,000 | | .748 | .696 | .798 | .803 | .811 | .806 | .830 | .785 | .778 | .763 | .757 | |
| 27,000 | | | | | | | | | | | | | |
| 30,000 | | .670 | | .770 | .782 | | .801 | | .757 | .749 | .732 | .721 | .704 |
| 40,000 | | .644 | | .727 | .748 | | .778 | | .700 | .700 | .684 | .665 | .647 |
| | | | | | | | | | {.653 | | | | |
| 50,000 | | .620 | | .692 | .722 | | .750 | | {.736 | .660 | .647 | .620 | .603 |
| 60,000 | | .599 | | .662 | .699 | | .723 | | .706 | .627 | .615 | .583 | .570 |
| 70,000 | | .581 | | .638 | .679 | | .699 | | .679 | .598 | .589 | .552 | .543 |
| | | | | | | | | | | {.572 | | | |
| 80,000 | | .566 | | .617 | .660 | | .678 | | .655 | {.644 | .566 | .526 | .521 |
| 90,000 | | .552 (a) | | .600 | .643 | | .657 | | .633 | .638 | .545 | .506 | .502 |
| 100,000 | | .534 | | .584 | .628 | | .638 | | .615 | .631 | .525 | .489 | .487 |
| | | | | | | | | | − △V/Vo | | | | |
| | | | {.0130 | | | | | | | | | | |
| 5,000 | | .0131 | {.0169 | .0127 | .0125 | | .0120 | | .0114 | .0114 | .0113 | .0109 | .0118 |
| 10,000 | | .0247 | .0284 | .0239 | .0238 | | .0230 | | .0225 | .0219 | .0215 | .0210 | .0224 |
| 15,000 | | .0355 | .0390 | .0340 | .0342 | | .0334 | | .0320 | .0318 | .0311 | .0302 | .0323 |
| | | {.0448 | | | | | | | | | | | |
| 20,000 | | {.0486 | .0491 | .0438 | .0437 | | .0431 | | .0423 | .0414 | .0402 | .0390 | .0414 |
| 25,000 | | .0584 | | .0530 | .0528 | | .0524 | | .0516 | .0508 | .0485 | .0473 | .0499 |
| 30,000 | | .0671 | | .0615 | .0615 | | .0612 | | .0600 | .0595 | .0561 | .0550 | .0579 |
| 35,000 | | .0754 | | .0694 | .0698 | | .0695 | | .0673 | .0679 | .0636 | .0624 | .0650 |
| 40,000 | | .0829 | | .0753 | .0771 | | .0770 | | .0757 | .0756 | .0701 | .0690 | .0718 |

(a) Cusp in this interval.

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the time of reading, and if a longer time had been taken somewhat different readings would have been obtained. The initial effect of the addition of small amounts of lead to bismuth is to increase the proportional increase of resistance under pressure, $\frac{1}{R_0}\frac{dR}{dp}$, as shown in the table. This relative increase persists over the entire range up to 25,000, where the discontinuous transition to the II phase of bismuth occurs, but there are systematic differences compared with pure bismuth. For the latter, the curve of resistance against pressure is concave upward over its entire extent. The curve for 0.1 per cent Pb begins with slight but recognizable upward curvature, but presently between 10,000 and 15,000 there is a reversal, and there is marked downward curvature at the upper end near 25,000. At 0.2 and 0.5 per cent Pb the same initially greater rate of increase than for pure bismuth and the same upward curvature persist, but the reversal of curvature comes at successively lower pressures, and there is crossing with the curve for relative resistance of pure bismuth, the crossing occurring at 21,000 kg/cm$^2$ for 0.2 Pb and at 13,000 for 0.5 Pb. At 1.0 per cent Pb the initial rate of rise has dropped below that of pure bismuth, and the curve is everywhere concave downward. From 5 per cent Pb on, the curve of relative resistance falls from the start, always with downward curvature. Further, with increasing lead content another phenomenon appears, at first only at pressures close to 25,000, but with increasing lead content spreading to lower pressure and becoming more prominent. This phenomenon is a downward drift of resistance, the interpretation of which is assumed to be the irreversible appearance of the delta phase. With 0.1 Pb content this drift first appeared at a pressure of 24,500. With 2.5 Pb the drift was already perceptible at 15,000. This remained a fairly well defined lower limit of drift. Up to 60 per cent Pb drift always appeared at 15,000 and never as low as 10,000. No effort was made to define the limits more precisely between 10,000 and 15,000. The drift is sluggish, and at any fixed pressure tends to slow down, not, however, reaching a steady value in times practical to wait for. The rate of drift is in general greater at the higher pressures. The direction of drift of resistance remained down up to 60 per cent Pb; this is the opposite of the direction of the corresponding drift in the bismuth – tin

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system, and made more difficult the separation of the formation of delta from the bismuth I – II transition.

Beyond 25,000 the whole qualitative picture is abruptly altered by the appearance of the two bismuth transitions. These transitions apparently are associated with, and occur in, the alpha phase. The first transition, from I to II, occurs at about 25,300 kg/cm$^2$, and is associated with a large drop of resistance, which in the case of the 0.5 Pb composition, is by a factor of 20. In the neighborhood of 27,000 the transition from II to III occurs, accompanied by an *increase* of resistance (abnormally, against the direction of volume change), by a factor between 2 and 3 for small lead content, the factor becoming less with increasing lead. At the composition 37.5 per cent Pb there was only a vestigial trace of the II – III transition with increasing pressure, and with decreasing pressure all trace had completely disappeared. This is the principal argument for setting the boundary of the delta phase in the neighborhood of 37.5 per cent Pb.

The II – III transition phenomena were always clean cut at all compositions, with no drift or marked hysteresis, indicating no solution effects, and suggesting that the II and III phases are pure bismuth. If the specific resistances of the II and III phases at 27,000 and 30,000 respectively are plotted against composition Figure 4 will be obtained. There is considerable scatter of the individual points, but the general interpretation would not seem to be open to much doubt. In the pressure range of stability of modification II the system consists of a mixture of pure II and delta, resistance increasing from roughly $25 \times 10^{-6}$ for pure II to $60 \times 10^{-6}$ for pure delta. In the pressure range of stability of the modification III the system consists of a mixture of pure III and delta, the resistance decreasing from roughly $70 \times 10^{-6}$ for pure III to $60 \times 10^{-6}$ for pure delta. The irregularity of the points at the low lead end of Figure 4 probably does not have any deep significance. It is to be remembered that pure bismuth itself does not show consistent values for the ratio of the resistances of the various modifications, or for the ratio of resistance at 30,000 to that at atmospheric pressure. Part of the irregularity is doubtless due to the fact that bismuth is markedly non-isotropic, so that the average orientation of the grains will affect the result, and partly also because the I – II and II – III transitions are not reversible in the sense

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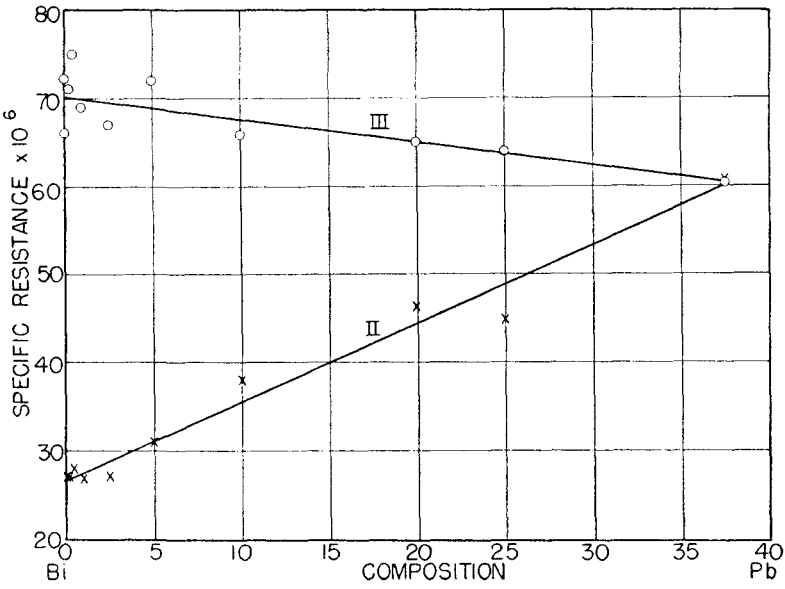


Figure 4. The specific resistances of the II and III phases of the system bismuth – lead as a function of gross composition in atomic per cent. The curve for II is at a pressure of 27,000 kg/cm², and the curve for III at 30,000.

that the original crystal orientation is recovered. A specimen originally in the form of a single crystal is transformed by an application and release of 30,000 kg/cm² into a multicrystalline aggregate with much distortion and offsetting of the grains, and a change of over-all dimensions, which may be in either direction. In three different set-ups with pure bismuth the values 6.34, 8.44, and 7.65 were obtained for the ratio of resistance of I to II at 25,000, the values 2.62, 2.67, and 4.12 for the ratio of the resistance of III to II at 27,000, and the values 0.606, 0.524, and 0.901 for the ratio of the resistance at 30,000 to that at atmospheric pressure. The first of the above three specimens was a single crystal; the two others were multi-crystalline extruded wire.

On release of pressure below 25,000 for compositions below 37.5 Pb new complicated phenomena appear. At first, on releasing pressure from the II phase to just below, say to 24,000 kg/cm², there is an abrupt and discontinuous rise of resistance due to the disappearance of the II phase. The resistance thus reached at

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24,000 is materially less than on the first application of pressure, the explanation doubtless being that now the transformation to delta has been completed, whereas with increasing pressure there was always some alpha mixed with delta. The resistance at 24,000 is steady, with no drift. Gradually, with further decreasing pressure, upward creep of resistance makes its appearance. The drift is sluggish and no approach to a steady reading was ever attained. Furthermore, with further decrease of pressure the drift becomes less rapid again, approximately vanishing in some cases at pressures between 15,000 and 10,000. With still further decrease of pressure and at compositions up to about 25 per cent Pb drift, always upwards, reappears, until near 7,000 the drift becomes a sweep, like a first order transition. The resistance to which the sweep carries is less than the resistance at the same pressure on the initial application of pressure to the virgin material. Beyond 25 per cent Pb resistance is permanently increased to more than its initial value, the excess persisting until 69 per cent Pb, at the presumptive edge of the beta range. The sweep-like large increase of resistance near 7,000 is doubtless the final stage of something at least approaching a first order transition in the delta phase. The more indefinite drift phenomena around 20,000 may possibly be unmixing effects. The fact of a pressure transition in the delta phase is made exceedingly probable by the behavior on the second increase of pressure. A reverse sweep-like decrease of resistance is now found centering around 20,000. The pressure transition of delta is therefore not a clean cut thing, but is spread over a considerable pressure range, with much hysteresis. The possibility cannot be ruled out that there are other sluggishly formed high pressure phases in delta. Going back now to the first release of pressure, below 7,000, a reverse creep to smaller resistances sometimes appears. This creep, however, is a very minor matter compared with the creep at higher pressures, and might very well be due to slight changes with pressure of the solubility limits.

Superposed on the phenomena of drift are the intrinsic effects of changing pressure, which in many cases are markedly larger than the effects of drift, so that it is possible to get a picture of the pure pressure effects in the absence of internal changes. At low lead concentrations, within the presumptive solubility limits,

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the pressure coefficient of the system after the irreversible formation of delta is positive, but less numerically than for the virgin material. At higher concentrations the sign of the pressure coefficient becomes negative, as is normal for most metals. The relation between pressure and resistance is, however, far from linear, with a number of instances of maximum resistance, and probably more often than not abnormal downward curvature.

Next consider the resistances in the range between 30,000 and 100,000 kg/cm$^2$ for compositions up to 69 per cent Pb, the edge of the beta range. It is a disadvantage of the method that readings cannot be made with decreasing pressure, and also that the pressure is only approximately hydrostatic. Up to 37.5 per cent Pb, the presumptive edge of the delta region, the usual method of applying a correction to secure agreement with the readings by the other method in the 20,000 – 30,000 interval could not be applied because of the disturbances incident to the bismuth transitions. In this range the resistances above 30,000 were corrected by a simple multiplicative factor such as to secure equality in the resistances at 30,000 as given by the two kinds of run. In general, this method of correction introduces an apparent break in the slope of the resistance curve at 30,000 which is not physically real. Nevertheless, smooth curves were obtained varying consistently with composition. The presumption is therefore that no new modification was formed irreversibly by the higher pressures in this range of composition. The ratios of resistance at 30,000 to that at 100,000 cluster around the value 1.24. The ratio of resistance at 100,000 to that at atmospheric pressure varies widely. At first, with very slight addition of lead, this ratio drops abruptly from 0.74 for pure bismuth to a minimum of approximately 0.108 at 2.5 per cent Pb, from which it climbs back to 0.42 at 37.5 Pb. The initial steep drop is a consequence of the large change in the ratio of the resistances of modifications III and I brought about by slight additions of lead, and the long climb back to 0.42 is a consequence of the gradual disappearance of the bismuth transitions at the edge of the domain of delta. In the range from 37.5 to 69.1 per cent Pb, that is, the range of mixed delta and beta, a new phenomenon appears at high pressure. All four compositions in this range, 37.5, 45, 50 and 60 per cent Pb, showed a cusp between 85,000 and 90,000, at which the rate of decrease

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of resistance abruptly increased by a factor of 3 or 2. The cusp disappears at the beta edge of the range and is most marked for pure delta. The presumption is therefore that the cusp is associated with pure delta; it does not appear, however, at 25 per cent Pb as would be expected on this basis.

Consider now the effects of pressure on the resistance of compositions in the range from 69.1 to 100 per cent Pb, that is, the range of beta, mixed beta and gamma, and pure gamma. The resistance of the composition 69.1 per cent Pb under pressure is without hysteresis, single valued, and without seasoning effects on the initial application of pressure. It is therefore highly probable that this composition corresponds to a single phase, beta, and that the composition limits of the phase continue to include 69.1 up to a pressure of 30,000. The next two compositions, 75 and 80 Pb, do show hysteresis in the resistance, the hysteresis loop being nearly closed so that there is only small permanent change of resistance (an increase) after exposure to pressure. The increasing and decreasing loops are reproduced in Table V. There was no appreciable drift associated with this hysteresis. The probable explanation is a shift with pressure of the solubility limits. Because the hysteresis is markedly greater at 80 per cent Pb than at 75, it is probable that the greater part of any shift with pressure of the solubility limits is associated with the edge of the gamma region rather than with the edge of the beta region.

The remaining compositions, 85, 90, 95, and 97.5 Pb, are again single valued and free from hysteresis or seasoning effects. It is therefore probable that any pressure effects on the solubility limit of the range of gamma is not great enough to bring the composition 85 per cent Pb outside the homogeneous range under any pressure below 30,000. In the range 85 to 100 Pb the effects of pressure up to 30,000 are entirely normal, resistance decreasing under pressure with upward curvature, the numerical magnitude of the effect decreasing slightly with increasing lead content. At higher pressures the compositions 85 and 90 Pb show a new effect, a relatively large increase of resistance (that is, a change in the abnormal direction) with an abruptness that seems to indicate a first order transition. The pressure of this transition is 50,000 for 85 Pb and 80,000 for 90 Pb, that is, a pressure increasing with lead content. Linear extrapolation would indicate

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110,000 kg/cm$^2$ at 95 Pb, beyond the range of this work. Indeed no transition was found for 95 per cent Pb up to 100,000. The magnitude of the discontinuity varies little from 85 to 90 per cent Pb, suggesting that extrapolation is permissible to pure lead, and suggesting the surmise that pure lead will be found to have a transition with abnormal direction of change of resistance in the neighborhood of 150,000 kg/cm$^2$ at room temperature.

Except for the incidents mentioned, the resistances of the compositions from 69 to 100 per cent Pb are smooth in the pressure range above 30,000. It was possible to correct most of the readings in this range to secure agreement with the other measurements in the 20,000 – 30,000 range, so that the resistances given in the table should be fairly good. The table does indeed show a fairly regular progression of change with composition.

Next, the compressions in the range to 40,000 are to be considered. In the composition range from 69.1 to 100 per cent Pb, there are no discontinuities or other incidents, and the compressions are smooth single valued functions of pressure. This means that any changes in the solubility limits produced by pressure in the range of mixed beta and gamma have too small an effect on the compression to be measurable. The compressions in this range are sufficiently indicated in the table. There is in general a small decrease in compression on passing from pure beta to pure lead.

For compositions below 69.1 per cent Pb the compressions are complicated by the two phase transitions in the alpha phase, the irreversible production of delta, and the sluggishly reversible transition of delta. Volume is much less sensitive to these various changes than is electrical resistance, and for that reason no measurements of compression were attempted for the four most dilute solutions, through 1 per cent Pb, since no measurable difference was to be expected as compared with pure bismuth. The compressions at 2.5 per cent Pb are appreciably less than those for pure bismuth. At the high pressures the primary reason for this is that not all the volume experiences the I – II and II – III transitions. The compressions for this composition are shown in the table. Irreversible formation of delta at this composition was not great enough to have a measurable effect on the compressions, so that the compressions were essentially the same with increas-

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ing and decreasing pressure, and are so shown. With 5 per cent Pb, however, the volume changes due to the irreversible formation and the reversible transition of delta become appreciable, resulting in different compressions with increasing and decreasing pressure. This effect continues through the domain of delta, and in the table two columns, one for increasing and one for decreasing pressure, are shown for all compositions through 60 per cent Pb. It was not possible to treat the transitions in a consistent fashion over the composition range, such phenomena as hysteresis, overshooting, and sluggishness being so capricious that the phase relations at a fixed pressure were not a consistent function of composition. One of the major sources of confusion was the capricious beginning of the irreversible formation of delta and the impossibility of separating this cleanly from the transitions I – II and II – III. It is usually possible to infer from the succession of figures in the various columns what the various discontinuities refer to. With increasing pressure three figures are usually shown at 25,000. These are usually the compressions for the I, II, and III modifications of alpha. At the lower lead concentrations the change of volume listed for I – II also includes the contribution of so much of the irreversible transformation to delta as has run at that pressure. With higher lead concentrations, however, it was possible to disentangle a volume change due to the formation of delta at a pressure below the transition to II, and for compositions 37.5, 45, 50, and 60 per cent Pb double compressions are shown at 20,000 or lower. Ideally the I – II and II – III transitions should drop out of the picture beyond 37.5 Pb, the presumptive composition of pure delta. Actually, however, this did not occur until 60 per cent lead was reached. Apparently, complete transformation to delta is certain only out of phase III, there being entangling effects in phases I and II which prevent the complete transformation and result in capricious variations, as shown, for example, by the irregular variation of the discontinuity at 25,000 for compositions 45 and 50 lead.

With release of pressure the III – II and II – I transitions are run through in reverse, and are shown usually at 25,000. The volume discontinuities with decreasing pressure differ from those with increasing pressure by the total amount of the irreversible formation of delta. Since the volume discontinuity II – III is in

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general less with decreasing pressure than with increasing, this shows that complete formation of delta does not occur from either phase I or II but requires the appearance of III for completion. The 25,000 discontinuity, that is, the I – III discontinuity, has completely disappeared with decreasing pressure at 37.5 Pb, as it should if this is the composition of the delta phase, as supposed. Consistent with this is the fact that if the total I – III discontinuity is plotted as a function of pressure, a series of points will be obtained which roughly extrapolate to zero at 69 per cent Pb with increasing pressure, and to 37.5 Pb at decreasing pressure. 69 per cent is the assumed composition of beta, the limiting composition of the system which can contain alpha with increasing pressure, and 37.5 is the composition of delta, the limiting composition of the system which can contain alpha with decreasing pressure. (It is to be remembered that I, II, and III pertain only to alpha.) On further release of pressure beyond the I – II – III region the pressure transition of delta appears. This is shown in the table as occurring uniformly at 5,000. This exact pressure is a conventionalization, the transition actually being smeared out through a region the limits of which did not vary consistently with composition. Between 37.5 and 69 per cent Pb the volume discontinuity at 5,000 is a roughly linear function of composition, running from a maximum of 0.0268 at 37.5 Pb to zero at 69. This is what is to be expected if within these limits the system consists of a mechanical mixture of delta and beta. Below 37.5 Pb the volume discontinuities also vary roughly linearly with composition. However, the discontinuities below 37.5 Pb are too low by a factor of 2 or 3 to connect with discontinuities above 37.5. The resistance measurements have already shown that the entire region below 20,000 with decreasing pressure is a region of incomplete internal equilibrium and slow drift. It would seem probable that the explanation of the failure of the volume discontinuities at 5,000 above and below 37.5 per cent Pb to connect with each other is due to the greater effectiveness of the alpha phase as compared with the beta phase to act as a catalyzer of the delta transition, so that there is less hysteresis and a smaller part of the transition is left for the final sweep near 5,000. This means that in the pressure range below 20,000 with decreasing pressure part of the apparent volume compression is actually due

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to the sluggish running of the delta transition, the error from this effect being greater in the presence of the alpha phase than in the presence of beta.

Finally, consider the shearing phenomena. The shearing curves start out at the bismuth rich end very similar to those for pure bismuth. The maximum and minimum characteristic of the I – II – III bismuth transition occurs for 2.5, 5, and 10 per cent Pb with diminishing amplitude, and at 20 Pb has become a point of inflection. The upper maximum and minimum between 60,000 and 70,000 characteristic of pure bismuth occurs also with diminishing amplitude, becoming a point of inflection and eventually disappearing above 25 per cent Pb. At 37.5 per cent Pb, pure delta, the curve retains only a trace of the lower bismuth episode, and the shearing strength reaches its maximum for the series. At 50 Pb all episodes have disappeared and the shearing curve is nearly linear with slight curvature in the normal direction. No high pressure shearing episode was found at the compositions 37.5, 45, 50, and 60 per cent Pb corresponding to the cusp in the resistances. At 69 Pb (pure beta phase) the curve is practically linear. At 75 Pb there is slightly more pronounced downward curvature. At 80 Pb, the first of the compositions at which the resistances indicated the appearance of a new high pressure phase, there is a slight maximum and minimum in the shearing curve to mark it. At 85 and 90 per cent Pb this is replaced by a point of inflection with rising slope, and the lowest values of shearing strength in the series are reached, at about 65 per cent that of pure lead. At 95 Pb the curve is nearly linear with slight downward hook at the very top (incipient appearance of the transition?) and at 97.5 Pb the curve is nearly linear with slight abnormal upward curvature over the entire length. The absolute shearing strengths at 80,000 kg/cm$^2$ in order, beginning at the bismuth rich end, are respectively: 1,020, 1,090, 1,200, 1,270, 1,040, 1,340, 1,300, 1,280, 1,200, 1,010, 950, 940, 770, 770, 960, and 1,200 kg/cm$^2$. The shearing curves for the compositions 37.5, 45, and 60 per cent Pb were measured to 100,000 instead of 80,000. No new episodes appeared above 80,000, the curves continuing to rise at the expected rate.

*Bismuth – Indium.* There have been two investigations of the phase diagram of this system since the publication of Hansen's

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book which essentially alter the picture of the behavior of this system. These investigations are by Henry and Badwick[12] and by Peretti and Carapella.[13] The phase diagram of the latter is reproduced in Figure 5. There are two intermetallic compounds, $In_2Bi$ and InBi, and, correspondingly, the system is the most complicated of any of the systems containing bismuth yet investigated in this program. At room temperature the diagram of Peretti and Carapella would lead one to expect the following: a homogeneous alpha phase of the same lattice as pure indium running from pure indium to perhaps 5 per cent bismuth, a mixed alpha and beta phase running to about 33.3 per cent Bi, a very narrow beta phase the same as $In_2Bi$ centering around 33.3 Bi, a mixed beta and gamma phase running to approximately 50 Bi, a very narrow gamma phase, the same as InBi, centering around

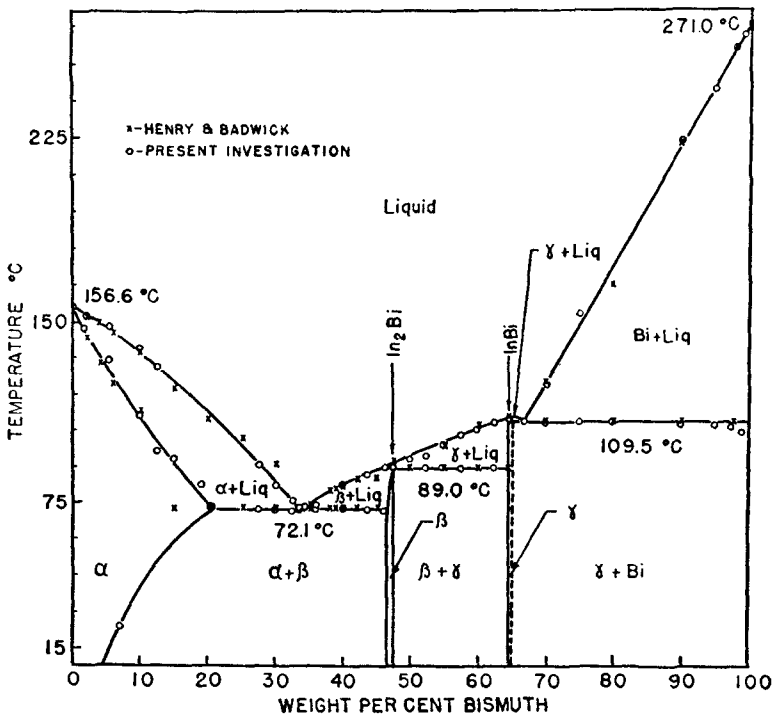


Figure 5. The phase diagram at atmospheric pressure of the system bismuth — indium according to Peretti and Carapella.

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50 Bi, and a mixed gamma and delta phase (pure bismuth) running to approximately pure bismuth. The diagram of Peretti and Carapella does not suggest appreciable solubility of indium in bismuth.

In the present work 25 compositions were investigated in addition to the pure metals. Weighed quantities of the metals were melted together in evacuated pyrex and quenched, as usual. After casting an additional step was sometimes employed, namely rolling the slug at room temperature to a thin strip, cutting into small pieces, thoroughly mixing the pieces, and remelting. After this, in almost all cases the specimens were subjected to a temperature annealing for 15 or more hours. The annealing temperature was 100° (boiling water) for compositions from 100 to 50 per cent Bi, 84° (boiling ethylene chloride) for compositions in the beta plus gamma range, and 68° (boiling sec-butyl chloride) for compositions in the alpha plus beta range. There was no definite evidence that these elaborate precautions were necessary. All the alloys were soft and the resistance specimens were extruded at room temperature.

Before describing the results in detail it will pay to briefly indicate their general nature. In the composition range from 100 to 50 per cent Bi, where the system presumably becomes all InBi, the two bismuth transitions persist, vanishing at the lower edge. The pressure of these transitions remains little affected through this entire composition range. Superposed on these transitions is an irreversible transformation of some kind which makes its appearance on first application of pressure in the neighborhood of 25,000 and is difficult to separate from the first bismuth transition because both are accompanied by a drop of resistance. The new irreversible form has itself a sluggish reversible transition on release of pressure in the general neighborhood of 20,000. This form is unstable and slowly reverts to presumably the original form on standing at room temperature. The creep phenomena in the entire region between 100 and 50 per cent Bi are unusually complicated and will be described in detail later. In the domain from 50 to 36 per cent Bi the phenomena are simple, with no transitions, and with single valued relations between pressure and resistance or volume. The narrow region from 36 to 33.3 per cent Bi inclusive is a region of new complication. On

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first increasing pressure there is at 20,000 a large abrupt increase of resistance, which persists up to 30,000 (and 100,000) and back to 8,000, where there is an abrupt drop, but not back to the original value. The phase thus formed is unstable with respect to the original, and in the pressure range from 8,000 back to atmospheric pressure there is continual creep with presumptively complete recovery of the original form on standing a sufficient time at room temperature. On passing from 33.3 to 32.3 per cent Bi the complications abruptly disappear and resistance and volume are again single valued in pressure. At 31.1 per cent Bi resistance is double valued in pressure between 8,000 and 23,000, but single valued over the rest of the range. A similar episode appears at 25 Bi, but less marked. Beyond 25 Bi resistance and volume again are smooth and single valued in pressure with no creep phenomena on changing pressure at constant temperature. There are, however, creep phenomena in the resistance on lowering temperature from room temperature to 0° and back to room temperature. This is doubtless an effect of the very definite variation with temperature of the solubility limits of bismuth in indium shown in the phase diagram of Peretti and Carapella.

The densities at atmospheric pressure as a function of composition are shown in Figure 6. There is a break in direction at 50 – 50 (BiIn) and a much less certain break at 33.3 Bi – 66.7 In ($BiIn_2$). The two compounds are formed from the elements with marked contraction of volume. The density of BiIn calculated on the basis of simple additivity of volumes is 8.41 against 8.95 actual. The corresponding figures for $BiIn_2$ are 8.00 against 8.40 observed. Within the limits of error there seems to be no consistent variation of density as measured before and after the application of 40,000 kg/cm$^2$; this means that the volume of any phase formed irreversibly by the action of pressure is not perceptibly different from that of the virgin material.

The specific resistance at atmospheric pressure is shown in Figure 7. Four definite ranges are recognizable: from 100 to 50 Bi, from 50 to perhaps 37 Bi, from 37 to 33.3 Bi, and from 33.3 Bi to 100 In. There would seem little room for doubt of the reality of the narrow range between 37 and 33.3, which is confirmed by the behavior under pressure. This range is not suggested by the diagram of Peretti and Carapella.

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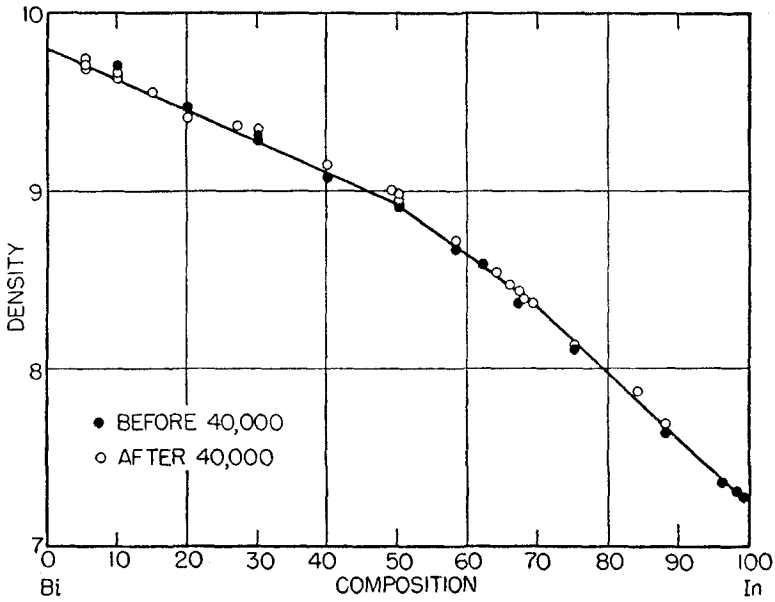


Figure 6. Density at atmospheric pressure and room temperature of the system bismuth – indium as a function of composition in atomic per cent.

Between 50 and 100 In there is no consistent indication of a difference in resistance before and after the application of pressure. In the domain up to 50 In, however, the effect is marked in spite of considerable irregularity in the points. At the bismuth rich end the resistance after pressure is definitely greater than before pressure, but the precise amount of the difference is made indefinite by the effect of creep. At the extreme bismuth end, the resistance of the dilute solutions is definitely greater than that of pure bismuth. This would seem to indicate appreciable solubility of indium in bismuth, to the extent perhaps of one per cent. The effect of dissolved indium on resistance is not large, however, being of a lower order of magnitude than that of dissolved tin, for example. The phase diagram of Peretti and Carapella should probably be amended by the addition of a zone of slight solubility.

The temperature coefficients of resistance at atmospheric pressure are shown in Figure 8. At the bismuth rich end the

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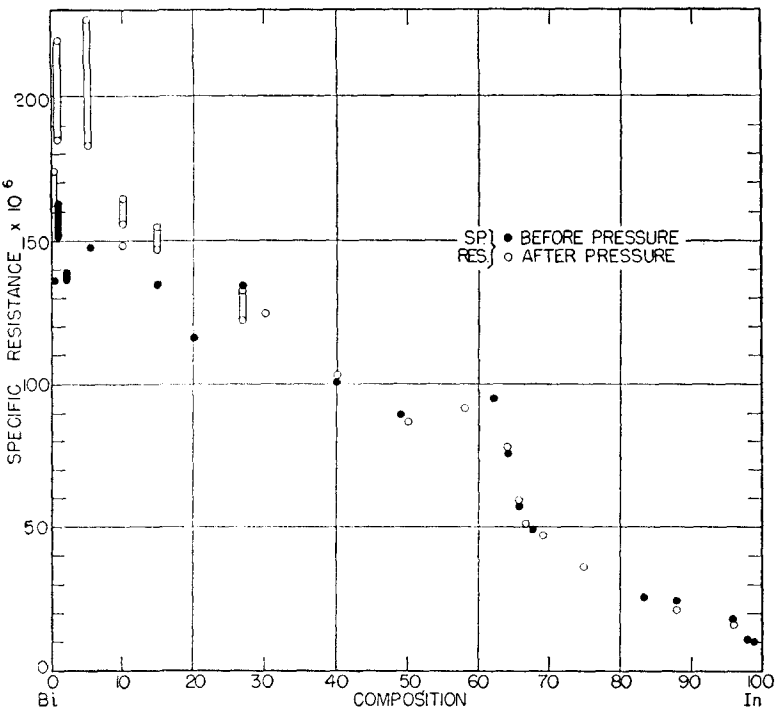


Figure 7. Specific resistance at atmospheric pressure of the bismuth – indium system, before and after exposure to pressure as a function of composition in atomic per cent.

effect of a slight addition of indium is a large drop in temperature coefficient, the effect being much greater than on the specific resistance. In this range the coefficient after the irreversible transformation produced by exposure to pressure has become negative. Measurement of these coefficients may sometimes be affected by running of the reverse transition during the measurement. For example, the coefficient –0.00185 given for 99 Bi – 1 In was measured immediately after the pressure run and is too large numerically because of appreciable reversion to the virgin form during the temperature cycle, but the value –0.00060 was measured on the same specimen after the lapse of four days, when there was no measurable change of resistance during the temperature cycle. After the minimum coefficient in the neighbor-

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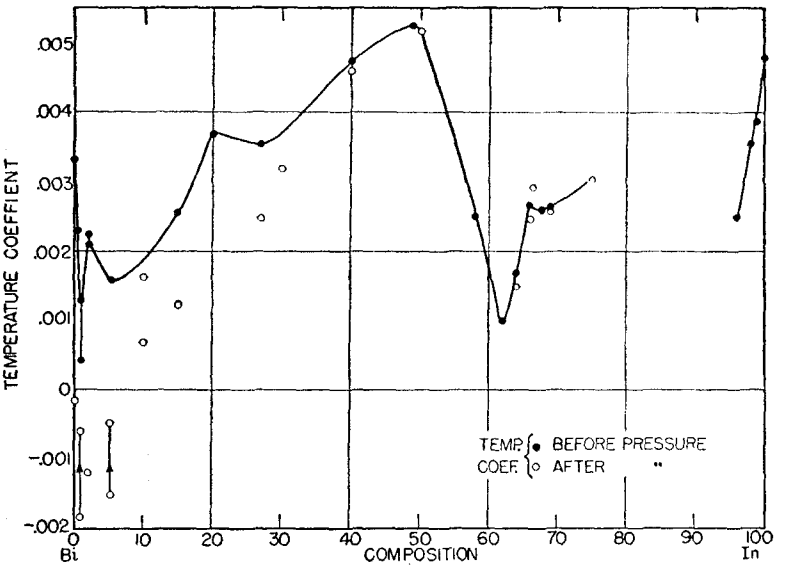


Figure 8. The temperature coefficient of resistance at atmospheric pressure of the bismuth – indium system, before and after exposure to pressure, as a function of composition in atomic per cent.

hood of 1 or 2 per cent In, the coefficient climbs with composition to a sharp maximum of 0.0052 at composition 50 – 50, a value higher than that of either pure component, suggesting that BiIn is a truly *metallic* compound. Beyond 50 –50 there is a steep drop in coefficient to a sharp minimum near 62 per cent In, correlated with the behavior of resistance, then an abrupt rise in the narrow domain reaching to 66.7 In, again correlated with the behavior of resistance. In the domain beyond 66.7 In there is at first a rise in the coefficient, but presently at 83.3 and 88 In the measurements of temperature coefficient are vitiated by drift of resistance during the temperature cycle. (The error introduced into the specific resistance by this drift is much less.) Finally, from 96 to 100 per cent In the drift during the temperature cycle disappears, and the values of the coefficients are depressed below that of the pure metal in the way to be expected of a solution. The fact that drift has disappeared in this range doubtless means that from 96 to 100 In we are in the range of homogeneous solution, consistently with the diagram of Peretti and Carapella.

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Table VI gives a summary of the numerical results. It is not possible to compress into a table of this sort a complete description of all these complex phenomena, and the entries in the table must be taken (in the ranges where there is drift and incomplete internal equilibrium) as only indicative of the general nature of the effects. In general, the two columns of the table for resistances below 30,000 indicate values obtained with increasing and decreasing pressure. The two values for resistance at atmospheric pressure on release of pressure are values obtained immediately after the pressure run and after waiting for some time. The table will have to be supplemented by verbal description, which now follows.

For the composition 99.5 per cent Bi an abrupt drop in resistance, marking the appearance of Bi II, occurred between 25,300 and 26,300, with no preliminary drift. Phase III appeared between 27,300 and 30,000. During the return cycle pressure was released directly from 27,400, where the system is in phase III, to 23,800; here the new phase appeared abruptly, with large increase of resistance. At this pressure the drift of resistance was from the first *down*. Drift *up* would instead be expected if this transition is like the transitions usually encountered, the drift being upward because of incompletion of the transition. The fact that the drift is paradoxically downward doubtless means that the transition to the new phase was complete in one sweep, and the new phase immediately starts its slow irreversible return to the original Bi I. This downward creep was perceptible all the way down to atmospheric pressure, becoming somewhat more rapid at the lower pressures, but nowhere being rapid enough to make the settings on resistance difficult. The two figures given in the table for the relative resistance at atmospheric pressure, 1.26 and 1.16, mark the amount of reversion on standing at room temperature for 8 hours. The next composition, 99 per cent Bi, gave smooth readings with no drift on the initial application of pressure up to 25,200. Notice, however, that the table shows that the upward curvature of 100 and 99.5 Bi has reversed at the upper end of the range, there being a point of inflection near 15,000. The abrupt discontinuities marking the appearance of II and III were both found with increasing and decreasing pressure, the resistances of these phases being single valued in pressure. However, the II

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# TABLE VI

## Bismuth — Indium

| | | 100 Bi | 99.5 Bi 0.5 In | 99 Bi 1 In | 98 Bi 2 In | 94.53 Bi 5.47 In | 90 Bi 10 In |
|---|---|---|---|---|---|---|---|
| Density | Before | 9.81 | 9.81 | 9.80 | 9.78 | | 9.68 |
| | After | | | 9.79 | 9.72 | 9.67 | 9.67 |
| $\rho_{00} \times 10^6$ | Before | 131 | 136 | 151 | 137 | 147 | |
| | After | 126 | 174 | 220, 185 | 203 | 183, 222 | 148, 164 |
| Temperature Coefficient | Before | .00331 | .00227 | .00130, .00040 | .00209, .00222 | .00159 | |
| | After | .00326 | −.00016 | −.00185, −.00060 | −.00120 | −.00154, −.00048 | .00069, .00165 |
| Pressure kg/cm² | | | | | Rp/Ro | | |
| 0 | | 1.000 | 1.000 {1.16 1.26 | 1.000 {1.22 1.46 | 1.000 {1.19 1.32 | 1.000 {1.19 1.39 1.63 | 1.000 {1.15 1.30 |
| 5,000 | | 1.098 | 1.102 1.48 | 1.109 1.73 | 1.108 1.58 | 1.093 1.96 | 1.074 1.47 |
| 10,000 | | 1.210 | 1.225 1.69 | 1.237 1.99 | 1.228 1.85 | 1.197 2.24 | 1.154 1.59 |
| 15,000 | | 1.335 | 1.364 1.88 | 1.380 2.19 | 1.365 2.06 | 1.302 2.47 | 1.235 1.68 |
| 20,000 | | 1.474 | 1.509 2.02 | 1.530 2.3 | 1.494 {2.22 1.89 | 1.413 2.53 (a) 1.29 (b) | 1.303 1.73 .94 (c) |
| 25,000 | | 1.638 | {1.663 2.12 .203 | {1.654 2.4 .201 | {1.595 1.89 .209 | {1.319 .243 | {1.16 .426 |
| 27,500 | | | .545 | .520 | .513 | .519 | .544 |
| 30,000 | | .900 | .534 | .512 | .507 | .511 | .539 |
| 40,000 | | .867 | .513 | .494 | .491 | .492 | .520 |
| 50,000 | | .837 | .495 | .478 | .477 | .476 | .502 |
| 60,000 | | .811 | .479 | .464 | .463 | .461 | .485 |
| 70,000 | | .787 | .466 | .450 | .451 | .447 | .472 |
| 80,000 | | .764 | .454 | .438 | .440 | .436 | .460 |
| 90,000 | | .747 | .443 | .428 | .430 | .426 | .448 |
| 100,000 | | .730 | .433 | .418 | .421 | .417 | .438 |
| | | | | | − ΔV/Vo | | |
| 5,000 | | .0163 | | | .0151 | .0146 | .0150 |
| 10,000 | | .0290 | | | .0286 | .0278 | .0282 |
| 15,000 | | .0410 | | | .0408 | .0400 | .0402 |
| 20,000 | | .0520 | | | {.0521I .0531I′ | {.0514I .0536I′ | {.0516I .0595I′ |
| 25,000 | | | | | {.0629I .0645I′ .1092II .1432III | {.0618I .0641I′ .1055II .1365III | {.0621I .0704I′ .1043II .1305III |
| 30,000 | | .1526 | | | .1514 | .1453 | .1390 |
| 35,000 | | .1601 | | | .1588 | .1534 | .1471 |
| 40,000 | | .1670 | | | .1650 | .1603 | .1541 |

(a) At 17,500. (b) At 22,500. (c) At 23,000.

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## TABLE VI – *Continued*

### BISMUTH – INDIUM

| | | 85.13 Bi 14.87 In | 80 Bi 20 In | 73.06 Bi 26.94 In | 70 Bi 30 In | 60 Bi 40 In |
|---|---|---|---|---|---|---|
| Density | Before | 9.58 | 9.47 | 9.37 | 9.32 | 9.13 |
| | After | 9.56 | | 9.37 | 9.34 | 9.15 |
| $\rho_{00} \times 10^6$ | Before | 135 | 116 | 134 | | 100 |
| | After | 147, 155 | | 122, 133 | 125 | 103 |
| Temperature Coefficient | Before | .00255 | .00366 | .00353 | | .00473 |
| | After | .00120, .00123 | | .00246 | .00319 | .00458 |
| Pressure kg/cm² | | | | Rp/Ro | | |
| 0 | | 1.000 {1.15 / 1.31} | 1.000 1.33 | 1.000 1.15 | 1.00000 {1.07 / 1.18} | 1.000 1.017 |
| 5,000 | | 1.052 1.47 | 1.037 1.42 | 1.015 1.21 | 1.00084 1.22 | .974 .995 |
| 10,000 | | 1.113 1.58 | 1.065 1.49 | 1.033 1.24 | 1.00076 1.23 | .948 .971 |
| 15,000 | | 1.161 1.65 | 1.102 1.54 | 1.043 1.25 | .99898 1.24 | .914 .940 |
| 20,000 | | 1.196 1.71 | 1.114 {1.56 / .69} | 1.031 1.11 | .964 {1.22 / .64} | .874 {.900 / .701} |
| 25,000 | | .75 | .42 .54 | .81 [d] 0.415 .45 | .62 | .805 .657 |
| 27,500 | | {.298 / .579} .41 | .609 | 0.617 | | |
| 30,000 | | .569 | .597 | .602 | .595 | .619 |
| 40,000 | | .547 | .570 | .572 | .561 | .582 |
| 50,000 | | .526 | .547 | .547 | .532 | .548 |
| 60,000 | | .507 | .526 | .521 | .506 | .518 |
| 70,000 | | .491 | .509 | .499 | .484 | .494 |
| 80,000 | | .476 | .494 | .480 | .465 | .471 |
| 90,000 | | .462 | .480 | .463 | .448 | .452 |
| 100,000 | | .449 | .467 | .447 | .434 | .433 |
| | | | | $-\Delta V/Vo$ | | |
| 5,000 | | .0150 | .0144 | .0144 | .0149 | .0147 |
| 10,000 | | .0281 | .0273 | .0273 | .0281 | .0279 |
| 15,000 | | .0401 | .0387 | .0397 | .0400 | .0401 |
| 20,000 | | {.0515I / .0543I′} | {.0504I / .0623I′} | {.0512I / .0541I′} | {.0513I / .0573I′} | {.0516I / .0670I′} |
| 25,000 | | {.0624I .0657I′ / .0957II .1195III} | {.0611I .0963II / .1132III} | {.0615I / .0643I′} | {.0624I .0685I′ / .0848II .0983III} | {.0619I .0777I′ / .0802II} |
| | | | {.1048II / .1224III} | [k] {.0663I .0919II / .1070III} | .1074 | {.0885II / .0905III} |
| 30,000 | | .1277 | | .1203 | .1157 | .0994 |
| 35,000 | | .1358 | .1305 | | | |
| 40,000 | | .1434 | .1373 | .1275 | .1229 | .1070 |

(d) At 23,000. (k) At 27,500.

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# TABLE VI — *Continued*

## Bismuth — Indium

| | | 51.16 Bi 48.84 In | 50 Bi 50 In | 42 Bi 58 In | 38 Bi 62 In | 36 Bi 64 In | 34.3 Bi 65.7 In | 33.3 Bi 66.7 In |
|---|---|---|---|---|---|---|---|---|
| | Before | 8.98 | 8.91 | 8.66 | 8.59 | 8.54 | 8.47 | 8.37 |
| Density | After | 9.00 | 8.95 | 8.71 | | | | |
| | Before | 89.4 | | | 94.7 | 75.4 | 57.1 | |
| $\rho_{00} \times 10^6$ | After | | 86.7 | 91.0 | | 77.4 | 59.1 | 50.9 |
| Temperature | Before | .00523 | | | .00099 | .00167 | .00266 | |
| Coefficient | After | | .00513 | .00248 | | .00152 | .00243 | .00292 |
| Pressure kg/cm² | | | | | | Rp/Ro | | |
| 0 | | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 1.013 / 1.022 | 1.000 1.067 | 1.000 1.010 |
| 5,000 | | .952 | .947 | .958 | .971 | .965 1.030 | .954 1.081 | .952 1.047 |
| 10,000 | | .908 | .893 | .916 | .943 | .932 1.101 (g) | .907 1.264 (h) | .909 1.342 (i) |
| 15,000 | | .860 | .838 (f) | .872 | .917 | .904 1.070 | .879 1.223 | .871 1.295 |
| 20,000 | | .799 | .776 | .829 | .890 | .879 / 1.042 1.042 | .849 1.189 / 1.189 | .837 1.255 / 1.255 |
| 25,000 | | .725 | .715 | .786 | .866 | 1.015 1.015 | 1.159 1.159 | 1.220 1.220 |
| 27,500 | | | | | | | | |
| 30,000 | | .665 | .658 | .748 | .843 | .991 | 1.133 | 1.191 |
| 40,000 | | .601 | .593 | .685 | .815 | .960 | 1.109 | 1.062 |
| 50,000 | | .552 | .544 | .640 | .790 | .934 | 1.087 | .946 |
| 60,000 | | .513 | .506 | .599 | .768 | .912 | 1.067 | .865 |
| 70,000 | | .485 | .476 | .567 | .749 | .892 | 1.047 | .816 |
| 80,000 | | .461 | .450 | .539 | .733 | .874 | 1.029 | .784 |
| 90,000 | | .436 (e) | .427 | .514 | .717 | .855 | 1.011 | .763 |
| 100,000 | | .410 | .405 | .491 | .702 | .837 | .984 | .748 |
| | | | | | | $-\Delta V/Vo$ | | |
| 5,000 | | .0142 | .0140 | .0138 | .0132 | .0136 | .0134 .0147 | .0122 |
| 10,000 | | .0273 | .0270 | .0264 | .0250 | .0258 | .0255 .0270 | .0240 |
| 15,000 | | .0391I / .0417I′ | .0391 | .0379 | .0357 | .0368 | .0367 .0383 | .0350 |
| 20,000 | | .0502I / .0520I′ / .0607I | .0504 | .0483 | .0459 | .0469 | .0470 .0487 | .0452 |
| 25,000 | | .0628I′ | .0609 | .0579 | .0557 | .0569 | .0568 .0586 | .0553 |
| 30,000 | | .0725 | .0706 | .0675 | .0645 | .0662 | .0659 .0673 | .0646 |
| 35,000 | | .0818 | .0794 | .0766 | .0732 | .0749 | .0763 | .0740 |
| 40,000 | | .0902 | .0878 | .0847 | .0815 | .0830 | .0844 | .0823 |

(e) Cusp at 84,000. (f) Cusp. (g) Transition. (h) Transition at 9,000; 1.273 and 1.082. (i) Transition at 8,000; 1.362 and 1.108.

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# TABLE VI — *Continued*

## Bismuth — Indium

| | | 32.3 Bi 67.7 In | 31.14 Bi 68.86 In | | 25 Bi 75 In | 16.73 Bi 83.27 In | 12 Bi 88 In | 4 Bi 96 In | 2 Bi 98 In | 1 Bi 99 In | 100 In |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | Before | 8.39 | 8.38 | | 8.11 | 7.89 | 7.63 | 7.36 | 7.31 | 7.27 | 7.28 |
| Density | After | | 8.36 | | 8.14 | 7.87 | | | | | |
| | Before | 49.1 | 47.1 | | | 25.4 | | 18.2 | 10.9 | 10.1 | 7.85 |
| $\rho_{00} \times 10^6$ | After | 49.3 | 47.4 | | 35.9 | | 21.1 | 16.3 | 11.2 | | |
| Temperature | Before | .00259 | .00262 | | | .00369? | | .00247 | .00357 | .00387 | .00478 |
| Coefficient | After | .00255 | .00257 | | .00303 | | .00406? | .00244 | .00352 | | |
| Pressure kg/cm² | | | | | | Rp/Ro | | | | | |
| 0 | | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 |
| 5,000 | | .949 | .949 | .949 | .950 | .951 | .953 | .959 | .945 | .942 | .933 |
| 10,000 | | .906 | .907 | .919 | .919 | .913 | .915 | .924 | .899 | .892 | .877 |
| 15,000 | | .868 | .869 | .894 | .871 | .881 | .871 | .892 | .858 | .851 | .829 |
| 20,000 | | .834 | .835 | .857 | .838 | .852 | .852 | .863 | .822 | .813 | .786 |
| 25,000 | | .804 | .806 | .806 | .810 | .826 | .828 | .836 | .792 | .781 | .749 |
| 27,500 | | | | | | | | | | | |
| 30,000 | | .780 | .781 | | .785 | .802 | .805 | .813 | .764 | .752 | .716 |
| 40,000 | | .767 | .744 (j) | | .755 | .773 | .774 | | | | .666 |
| 50,000 | | .778 | .732 | | .732 | .749 | .749 | | | | .623 |
| 60,000 | | .789 | .722 | | .710 | .727 | .730 | | | | .585 |
| 70,000 | | .790 | .714 | | .692 | .710 | .713 | | | | .554 |
| 80,000 | | .784 | .705 | | .677 | .694 | .697 | | | | .526 |
| 90,000 | | .774 | .695 | | .663 | .680 | .683 | | | | .489 |
| 100,000 | | .762 | .681 | | .651 | .666 | .671 | | | | .473 |
| | | | | | | | $-\Delta V/Vo$ | | | | |
| 5,000 | | .0132 | .0136 | | .0128 | .0131 | .0126 | .0130 | | | .0127 |
| 10,000 | | .0253 | .0255 | | .0251 | .0247 | .0242 | .0244 | | | .0238 |
| 15,000 | | .0364 | .0360 | | .0359 | .0356 | .0344 | .0347 | | | .0341 |
| 20,000 | | .0466 | .0467 | | .0461 | .0457 | .0449 | .0447 | | | .0439 |
| 25,000 | | .0563 | .0565 | | .0559 | .0552 | .0545 | .0542 | | | .0532 |
| 30,000 | | .0652 | .0654 | | .0649 | .0641 | .0635 | .0627 | | | .0621 |
| 35,000 | | .0739 | .0737 | | .0741 | .0728 | .0723 | .0712 | | | .0708 |
| 40,000 | | .0821 | .0824 | | .0826 | .0806 | .0803 | .0793 | | | .0788 |

(j) Cusp.

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phase persisted down to 23,700, appreciably beyond the transition pressure in pure bismuth, thus showing an effect of the dissolved indium in spreading the limits of indifference. Between 23,700 and 23,200 the new irreversible phase abruptly appeared with large increase of resistance, and again the drift was immediately *down*. Pressure was released another thousand in two steps, drift continuing in the same direction, whereupon the direction of pressure change was reversed to an increase. Readings were now made at five pressures in the interval to 25,500; at all pressures the resistance was steady with no appreciable drift. Increase of pressure to 25,900 now gave the abrupt change to phase II, the resistance being exactly the same as on the initial appearance. Pressure was now released to 24,150, at which the abrupt rise of resistance appeared, but this time with no reverse drift. It is to be noticed that this pressure, 24,150, is 450 higher than the pressure at which the transition had not occurred on the initial cycle. That is, the previous occurrence of the transition decreases the width of the region of indifference for a second occurrence, a sort of memory effect that has been encountered in other instances. On further release of pressure, to 23,100, very slight drift down appeared, becoming greater at 22,000 and 21,000. The absolute values of resistance on second occurrence of the transition were approximately 4 per cent less than on the initial occurrence, unlike the transition to II, where the resistances on the two occurrences were the same. On further release of pressure to 19,000 the direction of drift unexpectedly reversed itself, the velocity upward now being about the same as the previous velocity downward at 21,000. Further release of pressure and readings at 17,000, 14,000, 10,000, 5,000, and zero all gave downward drift again, increasing in velocity with decreasing pressure. On standing at atmospheric pressure a recovery of relative resistance from 1.46 initial immediately after the run to 1.22 occurred in four days. It is to be noticed that the pressure coefficient of resistance of the new phase is positive and larger than that of pure bismuth, which in this respect is an abnormal metal. The effect is too large to be obscured by any effects of drift. It suggests itself, therefore, that the new irreversible phase is closely related to pure bismuth.

A further remark is to be made about these drifts of resistance

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in general. After every change of pressure there is always a secondary reaction, pressure drifting back toward the former value, and the temperature inside the pressure vessel also drifting. Both drifts are effects of equalization of the adiabatic temperature changes brought about by change of pressure. These drifts are encountered in all pressure work, and I have long been familiar with them. The persistence of these drifts depends on the details of the construction of the apparatus and on the absolute pressure. With the present apparatus these drifts usually vanish in five minutes or so. The drifts with which we are concerned here are in addition to the normal drifts. Because of the presence of the normal drift it is not possible to establish the direction of drifts due to changes of internal equilibrium immediately after changes of pressure, unless they are large.

Consider next the composition 98 Bi – 2 In. At first with increasing pressure resistance increases, but nearly linearly and with point of slight inflection near 10,000. At 23,000 drift downward has already set in, becoming more rapid at 24,000 and 25,000, followed by the catastrophic drop to phase II at 26,000. Increase of pressure to 30,000 gives the abrupt rise associated with III, which on release of pressure persists to 27,800, but at 26,000 is followed by the catastrophic drop to II, and to exactly the same value as with increasing pressure. That is, there is nothing irreversible as yet in the II and III transitions. On further release of pressure to 23,950 II persists without creep. On further release to 23,400 something new appears. There is the catastrophic increase of resistance found for the two more dilute solutions, but the increase is not by the expected amount, and there is no creep. Further release of pressure to 21,400 gives a practically unaltered resistance, but with detectible upward creep. Further release to 17,500 gives a further catastrophic increase. That is, the irreversible transition at this composition becomes resolved into two. After the reading at 17,400 the direction of pressure change was reversed to an increase. Resistance at first increases with increasing pressure, but without creep. Creep downward appears between 22,500 and 23,800, practically the same pressure as on the initial application. Pressure was now increased to 24,350, at which the transition ran by an amount perhaps one tenth of the expected total. Pressure was again reversed, resistance at first dropping

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without creep, but at 19,000 there was again a jump back to nearly the previous value. From here, pressure was released to zero, the resistances lying on a smooth curve, concave toward the pressure axis, with markedly greater slope than that for the virgin material, and with drift progressively increasing with decreasing pressure. At atmospheric pressure the recovery of zero indicated in the table took place in 12 hours.

The next composition is 94.53 Bi – 5.47 In. On the initial application resistance increases smoothly, nearly linearly, and without drift to 20,000. At 24,500 there is marked deviation from the line and pronounced downward drift. At 26,000 the full value of resistance for II is apparently attained. The transition to III now does not occur sharply, but at 27,400 there is sluggish upward drift, the resistance being predominantly that of II, and the full transition to III does not occur until 30,000. On lowering pressure III persists without creep at 28,000 and at 26,000 there is full recovery of the value for II. Release to 24,100 is accompanied by a jump upward, but again by less than the full amount, and by a less amount than for the 2 per cent composition. Reversal of pressure in several small steps to 25,800 and back again to 24,100 yields an approximately constant resistance, again establishing the two-stepped nature of the irreversible change. Further release to 22,500 produces a relatively large increase of resistance with upward drift, but the full catastrophic jump upwards occurs between this and 17,500. Again the drift is downward immediately after the jump up. From here to zero a curve of steeply falling resistance is followed, with increasingly rapid downward drift. At atmospheric pressure there is a recovery of relative resistance from 1.63 to 1.39 in 10 hours, and a further recovery to 1.19 after 24 more hours, 6 of which were spent at 100° to hasten the recovery. It would appear probable that complete recovery of the initial resistance for any of these alloys is a matter of a very long time.

Two different specimens of the next composition, 90 Bi – 10 In, were investigated, both in much detail. In the first set-up pressure was pushed to the full 30,000 and the drift phenomena on release of pressure carefully studied, pressure being released in 30 steps. The jumps characteristic of Bi II and III were obtained on this run. On the second set-up pressure was carried at first to only

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25,300, at which II was perhaps not formed at all. With this set-up an additional pressure cycle was performed, pressure being released to 7,500, raised back to 26,500, where the complete jump characteristic of II was apparently obtained, and then back to 20,000 in small steps, and then to zero in steps of 5,000 kg/cm$^2$. Readings were made at 35 different pressures on the second set-up.

It is now time to introduce a notation for the new phases. We will designate by I′ the phase which is formed irreversibly in the neighborhood of 25,000 on the initial application of pressure to the virgin material, and by I″ the phase formed out of I′ on release of pressure. At low concentrations we have seen that the formation of I′ is entangled with the formation of II. One of the objects of the detailed examination of the 90 — 10 composition was to find whether it is necessary that II appear before I′ can appear. The conclusion seems justified that II is not necessary, at least at concentrations of indium as high as 10 per cent. Drift downward, indicating the formation of I′, occurred at 23,400 on the second set-up, but not at 20,000. Pressure was raised in five small steps to 25,300, somewhat below the pressure of the appearance of II under normal conditions, but without the catastrophic drop associated with II, but with sufficient drift to have lowered the total resistance by 25 per cent. Pressure was now lowered, downward drift persisting but so slight as to leave total resistance little changed, until 21,500 was reached, where the drift reversed to upward, with a 30 per cent upward jump occurring between 20,500 and 19,800. This jump upward marks the appearance of I″, which thus has appeared without the probable preliminary formation of II. Pressure was now released to 7,500, the drift being downward (decomposition of I″?) at all pressures, where pressure was again reversed. There was now no drift at 23,000, but at 26,600 the full jump downward characteristic of II occurred. Release of pressure to 24,100 now gave a reverse jump upward, to the same value as previously given by I′. Further release resulted in the same sequence as before, at first slow drift upward, followed at 20,400 by the jump characteristic of I″. That is, we here have had I′ formed first without the preliminary appearance of II and then with it, and I″ forming out of the I′ thus produced irrespective of the previous history of I′. The I″ formed the second time appeared at a slightly higher pressure

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than on the first appearance, and the jump of resistance was somewhat greater, indicating more complete formation of I″. These two points of slight difference on the two appearances are consistent with previous experience that the appearance of a new phase is facilitated by a preliminary rehearsal. The values shown in the table for this composition were taken from the first set-up to the full 30,000. The drift of relative resistance at zero from 1.30 to 1.15 shown in the table occurred in 8.7 hours. On the second set-up the drift of resistance at atmospheric pressure after the run was 10 per cent in 14 hours.

With the next composition, 85.13 Bi – 14.87 In, again two specimens were studied. The second specimen, studied in much greater detail than the first, combined the pressure steps of the two specimens of the preceding composition. The results with the first specimen will not be specially described – in the common domain results were obtained indistinguishable from those obtained with the second. Pressure on the second specimen was raised at first to 30,000, released to 5,000, raised again to 26,500, and released to zero. Readings were made at 56 different pressures. This time a special effort was made, on the second application of pressure, to determine the first appearance of drift marking the appearance of I′. There was no drift at 23,000 and definite drift at 23,800. The details of the appearance of I′ on release of pressure were practically the same on the first release of pressure, coming immediately from II and III, as on the second release, when only II had been previously realized. The details of the appearance of I′ were the same both times, a stationary point at 23,000, preceded by drift upward at higher pressures (disappearance of II), and followed by drift upward again at lower pressures (anticipating the appearance of I″). Again the absolute resistance of I″ was markedly greater on its second realization. The drop of relative resistance shown in the table at atmospheric pressure from 1.31 to 1.15 occurred in 13 hours.

The next two compositions, 80 Bi and 73.06 Bi, present no features not to be anticipated from the progression shown by the preceding compositions. Pressure was raised to 30,000 on both compositions, resulting in the characteristic appearance of II and III. The step on the resistance curve marking I′ on release

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of pressure and the transformation of I′ into I″ occurs also much as before. The pure pressure effect on resistance in the low pressure range also follows the progression expected; resistance of both I and I″ increases under pressure, but by a diminishing amount, and the downward curvature increases, by such an amount that above 15,000 for composition 73.06 resistance decreases with increasing pressure. This decrease is not accompanied by drift and is not an anticipation of the appearance of I′.

Composition 70 Bi — 30 In was again studied in more detail, the concentration of indium being now sufficiently high to make the two bismuth modifications, II and III, tend to fade out of the picture. Pressure was raised to 30,000, released to 15,000, raised to 23,800, and released to zero in 41 steps. Resistance of the virgin specimen is nearly constant under pressure up to 15,000, beyond which there is a 3.5 per cent drop to 20,000. There is marked downward drift at 24,000, probably due to formation of I′, again marked downward drift at 26,000, probably marking formation of II, further large drop between 26,000 and 28,000, probably marking the completion of the formation of II. At 28,000 there is slight upward drift, probably marking formation of III out of II, and again slight upward drift at 30,000, but there is never the pronounced upward jump associated with the full formation of III, which was probably present only in small quantity, its full formation being prevented by the dissolved indium. On release of pressure resistance increases approximately linearly with pressure until at 20,000 it has reached nearly twice its value at 30,000. Creep is practically absent in this entire stretch of 10,000 kg/cm$^2$. The results are difficult to interpret because the slope of the curve is much greater than the slope of resistance of II (or III either) against pressure. Between 20,000 and 19,600 a catastrophic jump of resistance by a factor of 6 occurs, probably marking the appearance of I″. There is no intermediate step in resistance such as, at lower concentrations of indium, marked the appearance of I′. Pressure was next released from 19,600 to 15,200; the resistance increases about 2 per cent in this stretch, with a slight superposed downward creep. Pressure was now reversed back to 23,000 in 6 steps; resistance decreases approximately linearly with pressure by a total of 15 per cent, with accentuated downward creep at all points. Between

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23,000 and 23,800 there is a catastrophic downward jump to approximately the value at the same pressure on the previous excursion. Creep continues downward when pressure is released to 22,500, beyond which there is a reversal, at 21,800, of the direction of creep. Creep now continues upward until the catastrophic upward jump of resistance at 20,000 is reached, marking again the probable appearance of I'. Beyond this, creep continues downward back to atmospheric pressure. Here the drop of relative resistance from 1.18 to 1.07 shown in the table occurred in 14 hours. It is evident that between the compositions 73.06 and 70 some drastic change has taken place in the region above 20,000; the simplest description perhaps is that phases II and I' have got themselves entangled and lost their individuality.

With the next composition, 60 Bi — 40 In, the progressive change of character is carried further. Resistance now decreases from the start with increasing pressure, with downward curvature. Downward creep first appears at 23,000. From here to 30,000 the tempo of decrease of resistance is much increased, but drift is not pronounced. What drift there is is down. On release of pressure from 30,000 to 20,000 the same linear increase without drift occurs that was found for 70 Bi. Between 20,000 and 19,000 an abrupt upward jump of 40 per cent occurs. Pressure was now increased, giving a large downward jump at 23,000, and on reversal, an upward jump at 21,500. In general description, the several transitions found at lower indium contents have disappeared and are replaced by a single transition which is smeared over the general region between 20,000 and 30,000 on first application of pressure, but which is sharpened into the region between 21,000 and 23,000 on second application. On final release of pressure from 21,000 the original curve is displaced upward approximately parallel to itself by 3 per cent. Drift phenomena are inconspicuous over the entire final stretch from 20,000 down, and the creep of zero in 14 hours is of the order of only 1 per cent.

At the next composition, 51.16 Bi, the phenomena are completely altered. The large discontinuities have disappeared and the only trace left is a very obtuse upward cusp in the curve of resistance at 26,000. Two applications of 30,000 were made to this composition. On the first, between 10,000 and 25,000, there was hysteresis between the readings with increasing and decreas-

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ing pressure, amounting to a maximum of 4 per cent at 17,000. On the second application the hysteresis disappeared, the curve with increasing and decreasing pressure essentially reproducing the initial curve with increasing pressure. At a few points, near the beginning and near the end of the hysteresis loop on the first application of pressure, drift was perceptible, but elsewhere the readings were steady.

At 50 Bi – 50 In the readings were single valued, without drift. The resistance is a smoothly decreasing function of pressure, except for a very obtuse cusp with *downward* break in the tangent at 15,000. This composition represents the compound BiIn, which we have seen from the temperature coefficient to be strongly metallic in character. The decrease of resistance under pressure is that to be associated with a soft low melting metal, the relative resistance at 30,000, 0.658, being somewhat less than that of lead or indium, but notably greater than that of sodium.

The next two compositions, 42 Bi – 58 In and 38 Bi – 62 In, present no unusual features. Resistance is single valued and without creep. The resistance of the first is very nearly linear in pressure, with very slight downward curvature (abnormal) in the first half of the pressure range, and very slight reversal in the upper half. The resistance of the second composition is normally slightly concave upward over the entire range.

With the next three compositions, 36 Bi – In 64, 34.3 Bi – 65.7 In, and 33.3 Bi – 66.7 In, abnormalities abruptly reenter the picture. Consistent runs were made on two specimens of the latter composition. The abnormality is the same in character for the three compositions. On the initial application of pressure resistance decreases smoothly to 15,000 without creep. Between 15,000 and 20,000 a large upward jump of resistance occurs, which is completed in the neighborhood of 21,000. From 21,000 to 30,000 resistance decreases smoothly with approximately the same slope as below 15,000. On release of pressure the increasing curve is retraced back to 20,000. Below 21,000 the curve follows a smooth prolongation of the curve above 21,000, until a pressure is reached in the neighborhood of 8,000. Here an abrupt downward jump occurs, which, however, is not great enough to carry the resistance back to the initial curve. The creep phenomena on approaching the jump vary consistently with the composition.

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With 36 Bi no creep is perceptible between 20,000 and the jump except a slight downward creep at the last point, 8,500, just before the jump. At composition 34.3 Bi *upward* creep occurs at 12,500 and 9,300, reversing to downward creep at 9,100, just before the jump. With composition 33.3 Bi upward creep is perceptible already at 21,000 and continues down to and including 11,000 (this was observed at 8 different pressures), reversing to downward creep at 8,000, just at the edge of the jump. After the jump, creep continues downward in the range to atmospheric pressure. At atmospheric pressure the creep is rapid enough to carry the resistance back to approximately the initial value in times accessible to observation. The recovery of the 36 Bi composition was to within less than 1 per cent of the initial value on standing 3 days, and the recovery of the 33.3 Bi composition was equally complete on standing over night. The interpretation of the results would seem to be that the virgin alloy changes irreversibly to a new modification in the neighborhood of 20,000, and this modification itself has a pressure transition in the neighborhood of 8,000 to a form unstable with respect to the virgin alloy, to which it sluggishly reverts. The velocity of irreversible reversion was in this case great enough to cast doubt on the nature of the pure effect of pressure on the resistance of the low pressure form. The probability is, however, suggested especially by several readings on the 33.3 composition, that the resistance of the low pressure form would decrease normally with increasing pressure.

With the next composition, differing by only 1 per cent from the last, namely 32.3 Bi — 67.7 In, the abnormalities abruptly disappear, and the curve between resistance and pressure is smooth, single valued, without creep, and concave upward in the normal fashion.

With the next composition, little more than 1 per cent further on, namely 31.14 Bi — 68.86 In, a small abnormality reappears. With increasing pressure a smooth curve is obtained much like that of the preceding composition. With decreasing pressure the curve is at first retraced, but between 22,000 and 8,000 resistances are too high, the decreasing curve having the appearance of a blister superposed on the increasing curve. At the high pressure end of the blister creep is upward, readings are steady

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at the mid pressure of the blister, and below the mid pressure creep is downward. Below 8,000 the regular curve is resumed, and zero is exactly recovered. One is perhaps tempted to try to explain this effect as due to the same new modification that appeared at compositions between 36 and 33.3 Bi, the specimen being slightly inhomogeneous with a small inclusion of the critical composition. This I think, however, is not tenable, for the new phase should appear at 20,000 on the first increase of pressure, and not on release.

The next composition, 25 Bi — 75 In, shows a slight trace of the same "blister" as the preceding composition. The maximum width of the blister is here less than 1 per cent of the total resistance against 3 per cent for the preceding composition. In the table the blister has been ignored and resistance is shown as a single valued function of pressure.

The next five compositions, 16.73 Bi, 12 Bi, 4 Bi, 2 Bi and 1 Bi, are normal in every respect. Resistance is a smooth single valued decreasing function of pressure, with normal upward curvature. The effect of pressure on the resistance of the three most dilute solutions, 1, 2, and 4 per cent Bi, progressively decreases. This is consistent with the usual rule that addition of another element in solution increases *algebraically* the pressure coefficient of resistance. The fact that the resistances of the compositions 12 Bi and 16.73 Bi showed no creep at any pressure is informative. Both these compositions showed pronounced creep at atmospheric pressure on lowering temperature from room temperature to 0°. This was explained as an effect of the variation of solubility limit with temperature. The fact that no corresponding creep was observed with changes of pressure would mean that the solubility limits are not changed appreciably by pressure.

The discussion thus far has been of the variation of resistance under pressures up to 30,000 kg/cm$^2$. Little further discussion is required of the measurements under pressures from 30,000 to 100,000. With two slight exceptions, no new abnormalities were encountered in this range, and resistance is a smoothly decreasing function of pressure over the entire range of composition. Because of the many abnormalities in the region between 20,000 and 30,000 it was not possible to use the usual method of correcting the data to 100,000 so as to secure agreement with the other

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values in the range between 20,000 and 30,000. Instead, a simple multiplicative correction was applied to each series of readings so as to secure agreement between the relative resistances at 30,000 as given by the two sets of measurement. The result may sometimes be an apparent break in the tangent at 30,000 which is not real. However, I think any error from such an effect is much less than it would have been in the early days of my measurements of resistance to 100,000. With continued use of the method and constant attention to small details of procedure, some of which it would be difficult to describe, the measurements give me the impression of much increased reliability, as shown by the agreement of repetitions of the same experiment.

The two slight abnormalities in the resistance above 30,000 referred to in the last paragraph are: a slightly downward bending cusp at 84,000 for 51.16 Bi, and an upward bending cusp at 40,000 for 31.13 Bi. The latter may possibly be an effect of the delayed appearance of the abnormality found with the 30,000 apparatus at lower pressures and indicated in the table.

Next consider the compression phenomena. The results here are not nearly as sensitive as for the resistance. In particular, phenomena of creep were never observable and transitions which could be resolved into two by the resistance measurements are here smeared together as one. On the other hand, it is an advantage of the method, since volume changes are additive of the changes of the different parts of the whole, unlike changes of resistance, that the total volume discontinuity associated with any known phase change is a measure of the fractional part of the whole system taking part in that transition. In the range from 100 to 50 per cent Bi the volume discontinuities to be associated with the bismuth transitions from I to II and from II to III were definitely marked, the first with increasing pressure and the second with both increasing and decreasing pressure. The volume change with decreasing pressure to be expected from the bismuth I – II transition was not found, however, but a somewhat different value. This doubtless corresponds to the new phase irreversibly formed, but whether the phase is that designated above as I′ or I″ could not be established, for the transition from I′ to I″ was not resolved in the compression apparatus. In the table the phase is designated everywhere as I′. The probability is that this refers to

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I′ at 25,000 or higher and to I″ at 20,000 or lower, the volume difference between I′ and I″ being too small to detect.

If the volume difference at 25,000 between I and III or between II and III is plotted against composition a rather good straight line will be obtained crossing the axis in the close vicinity of 50 per cent Bi. This is consistent with the supposition that the system comprises in this range a mechanical mixture of the bismuth phase and the compound BiIn, as demanded by the diagram of Peretti and Carapella. The volume differences between I and I′ given in the table are, on the other hand, quite irregular as a function of composition. Delayed and smeared out transitions between I′ and I″ are probably responsible. A smeared out transition is going to falsify the apparent compressibility in the regions of ostensibly single phases, and this may well be the explanation of the minor irregularities in the progression of the compressions given in the table.

It is to be remarked that the volume difference between I and I′ at 51.16 Bi, where the bismuth transitions proper have dropped out of the compression phenomena, is larger than might be expected from the comparatively slight abnormalities shown by the resistance at the same composition.

Beyond the composition range from 100 to 50 per cent Bi the compressions are smooth and without feature except for the two compositions 34.3 Bi and 33.3 Bi. Notice in the first place that the composition 36 Bi, which has a marked upward jump in resistance near 20,000, shows no abnormality of compression. Composition 34.3 Bi has a small hysteresis, between 5,000 and 30,000, between volume with increasing and decreasing pressure, doubtless an effect of the transition shown by the large change of resistance. However, this transition is much more sluggish in the volume apparatus than in the resistance apparatus, the transition not appearing with increasing pressure until 30,000 is exceeded, and not running with decreasing pressure until pressure is reduced below 5,000. With composition 33.3 Bi the only abnormality found was a jump upward of relative volume by 0.0029 on releasing pressure just above 5,000. This jump is not indicated in the table; the figures given were obtained by smoothly extrapolating to zero the results with decreasing pressure and averaging with the results with increasing pressure. The fact

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that a discontinuity was obtained with decreasing pressure means that the transitions must have run somewhere with increasing pressure. No corresponding discontinuity could be detected, however, and the transition must have been smeared out over a wide interval. This will result in a distributed error in the compressions sufficient to integrate to 0.0029 over the entire interval. The distribution of compressions shown in the table, which lie somewhat below the compressions of the neighboring compositions on either side, would suggest that the major part of the error is at the low pressure end.

These results on compression do not facilitate the interpretation of the nature of the phase changes shown by the resistance in the narrow composition interval 36, 34.3 and 33.3 Bi. The diagram of Peretti and Carapella would lead one to expect that the manifestations of a phase change would be sharpest at the composition of the pure compound, Bi $In_2$, but this composition does not mark the maximum of the disturbances of volume.

Finally, consider the shearing phenomena. Shearing curves to 100,000 were determined for the following compositions: 90, 85, 80, 73.06, 70, 60, 51.16, 50, 42, 33.3, 31.14, 16.73 and 12 per cent Bi. In the middle of the composition range, from 73.06 through 33.3 inclusive, a shearing phenomenon appeared which is not common with alloys or pure metals, although it has been encountered a number of times. These compositions, particularly at the higher pressures, did not shear smoothly, but shear was accompanied by a feeling of light rubbing or grinding, and there were audible manifestations, mostly squeaking of various sorts, but once, with composition 33.3 at the top pressure, a pronounced hissing. The significance of these effects is doubtless that the compounds BiIn and $BiIn_2$ do not assume one of the crystal forms, such as cubic or hexagonal, which permit easy shearing, but the lattice is presumably one of the more complicated ones with a large unit cell.

There is a progressive change in the character of the shearing curve with composition. At high bismuth concentrations there are two sets of pronounced maximum and minimum, marking the bismuth transitions in the neighborhood of 25,000 and 65,000. With decreasing bismuth content the upper maximum and minimum fades out first, giving way to a point of inflection. The lower maximum and minimum is still well marked at 60 Bi, but

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at 51.16 Bi has disappeared, the curve being approximately linear over its entire length. Beyond 50 Bi there are few pronounced episodes: the curves are mostly linear to a first approximation, with slight upward curvature predominating to a second approximation, but with scattered points of inflection and reversal of curvature. The curve at 16.73 Bi is an exception, being strongly curved upward over its entire length. The curve for composition 33.3 is smooth, with no episode corresponding to the jumps of resistance.

The shearing strengths at 100,000 for the compositions in order as given in the next to the last paragraph were respectively: 2,160 (average of two nearly equal runs), 2,050, 2,750, 2,560, 3,820, 4,090, 2,600, 4,950, 2,650, 3,270, 3,200, 5,000, and 2,380 kg/cm$^2$. The progression is not always smooth within the limits of error. Notice particularly the large jump from 2,600 to 4,950 for compositions 51.16 and 50, and the large value, 5,000, for composition 16.73. It would suggest itself that there may not be a consistent variation with composition of the phases actually being operated on in the shearing apparatus, due to the sluggishness of some of the transitions. This possibility was also suggested by the measurements of compression. The possibility is also always to be kept in mind of new phases occurring only in cooperation with shearing stress.

## Summary and Discussion

Nine alloy systems containing bismuth have now been measured in this program – alloys with tin, cadmium and thallium in preceding papers in addition to the alloys with silver, indium, lead, antimony, tellurium and zinc in this paper. Of these the alloys with silver, cadmium and zinc present no special feature; any solubility of the alloying element in either the low or high pressure modifications of bismuth is slight, and the system behaves approximately like a mechanical mixture. The system Bi – Te was studied only in the compositions 0.25 and 1.00 atomic per cent Te. Considerable changes in the properties, both at atmospheric pressure and under pressure, are produced by these small amounts of tellurium. The changes are not in the direction usually associated with solubility effects, and it is possible that at higher concentra-

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tions some of the complicated effects shown by the other systems would appear.

The remaining five systems, namely the alloys with indium, lead, antimony, tin and thallium, all show unusual effects and a certain family resemblance in the irreversible production of new forms by pressure, although the details vary from system to system. Consider in the first place the dilute systems. The metallurgical phase diagrams suggest for most of these systems that there is some solubility in bismuth, but the limits of solubility are usually extremely indefinite. It would seem that the electrical parameters can give better information. Furthermore it would seem in general that in making a theoretical attack on this problem the behavior of dilute solutions would receive first attention. For two of the systems, Bi – Sn and Bi – Pb, the addition of a small amount of alloying element to bismuth produces dramatically large increases of specific resistance, four to six fold at the maximum for the addition of about 1 per cent. At the same time that specific resistance rises the temperature coefficient of resistance rapidly drops, reaching minimum negative values at concentrations of the order of 0.2 per cent, markedly different from the composition of maximum specific resistance. The phase diagram shows that it is essentially pure tin that goes into solution in the Bi – Sn system, whereas in the Bi – Pb system the solute is approximately Bi 30 – Pb 70. The dilute alloys with indium and thallium also exhibit an increase of specific resistance and a decrease of temperature coefficient, but by much smaller amounts. In the Bi – In system there is an approximately 15 per cent increase of specific resistance at 1 per cent In, beyond which the resistance drops again, and in the Bi – Tl system the maximum increase is also approximately 15 per cent at 2 per cent thallium. The temperature coefficients in these two systems decrease with increasing specific resistance and reach their minimum at approximately the composition of maximum resistance, as would be expected. The solutes in these two systems are BiIn, a true intermetallic compound, and something of the approximate composition $Bi_3Tl_2$.

The dilute antimony system is not in line with the others. The metallurgical diagram indicates unlimited mutual solubility. Small additions of antimony to bismuth produced little change in the

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electrical properties; in fact it is not certain that specific resistance or temperature coefficient is changed at all by additions up to 2 per cent. Beyond this there is a gradual and long spread out increase of specific resistance and decrease of temperature coefficient, reaching a turning point in the neighborhood of 30 per cent Sb, far beyond the turning point in the other systems. There would seem to be a high degree of similarity between the bismuth and the antimony atom under these conditions.

The pressure coefficients of the dilute solutions show wide variability. The pressure coefficients at low pressures of the dilute tin and lead solutions are much increased, the maximum increase, which is of the order of 50 per cent, occurring at concentrations in the neighborhood of 0.1 per cent. The dilute solutions of indium and thallium also show an increase of the initial pressure coefficient, extending over a wider concentration range and reaching a turning point in the neighborhood of 5 per cent. At pressures higher than a few thousand kg/cm$^2$ all these systems show marked deviations from linearity between pressure and resistance. There are complicated reversals and crossings which cannot be briefly summarized, and which almost certainly indicate the interplay of more than one mechanism.

Beyond the dilute solution range and beyond the initial few thousand kg/cm$^2$ the effects of irreversible changes produced by pressure increasingly enter. The behavior of the Bi – Sn system is perhaps the simplest in this regard. The intermetallic compound BiSn is irreversibly formed. This compound itself exists in two or more pressure modifications, and it is only the high pressure modification which can be formed out of the virgin eutectic mixture of bismuth and tin. The irreversible formation of BiSn takes place between 20,000 and 25,000 kg/cm$^2$ and the most important reversible transition to a low pressure modification at about 15,000. The low pressure modification is unstable with respect to the virgin system and slow reversion takes place at atmospheric pressure extending over many days. The volume relations are such in this system as to make possible a fairly clean cut interpretation of the experimental results. In the other systems the experimental relations are less clean cut and the interpretation more obscure. In the Bi – Pb system a new phase is also irreversibly produced by pressure, but its structure is more

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complicated than in the Bi – Sn system, the composition being somewhere in the neighborhood of 63 Bi – 37 Pb. The new compound, if compound it is, has a fairly certain first order transition in the neighborhood of 7,000 kg/cm$^2$. Above 7,000 there are complicated creep effects, which suggest with some plausibility the existence of other pressure transitions. At atmospheric pressure the irreversibly formed new phase is stable, unlike the behavior in the Bi – Sn system. The changes of electrical resistance which accompany the irreversible and reversible transitions are not simple and, in those cases where a parallelism may be set up with the Bi – Sn system, may be of the opposite sign.

In the Bi – In system irreversible transformations are also produced by the application of pressure and the transformation product itself may undergo reversible pressure transitions. These effects are in some way associated with the pure bismuth phase, for they vanish at 50 Bi – 50 In, where the system takes the form of the compound BiIn. Unlike the situation in the Bi – Sn and Bi – Pb systems it seems probable that the irreversibly formed phase does not have any definite composition, but is capable of existence over a range of composition. The creep phenomena in the range out to 50 In are exceedingly complex. At atmospheric pressure the irreversibly formed new phase is unstable, but complete reversion to the virgin form will take a very long time. Beyond the composition of these complexities new irreversibilities and transitions appear in a composition range only 3 per cent wide in the neighborhood of the compound $BiIn_2$.

In the Bi – Tl system all the irreversible complexities associated with bismuth disappear beyond approximately 30 per cent thallium, a composition which marks the presumptive edge of a homogeneous range in the ordinary metallurgical phase diagram. The new irreversibly formed phase has one well marked pressure transition in the neighborhood of 7,000 kg/cm$^2$, and possibly several others. Its initial formation does not seem to be tied up with the II modification of bismuth, as it is in some of the other systems, but may take place with appreciable velocities at pressures as low as 20,000. It was not possible to get consistent enough values for the changes of resistance and volume with pressure and composition to decide whether the new form has a definite composition, corresponding to an intermetallic compound, or whether

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it is indefinitely spread over a range, as appears to be the case in the Bi – In system. The new irreversibly formed phase is unstable at atmospheric pressure and partial reversion slowly takes place.

In the Bi – Sb system the pattern of irreversible effects is quite different from that in the other systems. They occur over the entire composition range and vary in a complicated way with composition. At the bismuth rich end the irreversible production of the new form and the reversible bismuth transitions to II and III become smeared together into a single irreversible change. It seems fairly certain that at room temperature this system cannot have an unlimited homogeneity range, as given by the metallurgical diagram, but there must be perhaps several intermediate structures.

I am indebted to Mr. Charles Chase for setting up the apparatus and to Mr. L. H. Abbot for preparing the specimens and making many of the measurements.

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# Miscellaneous Effects of Pressure on Miscellaneous Substances

By P. W. Bridgman

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## Introduction

In this paper I present miscellaneous data for various substances which were unpublished at the time of my retirement and which I will have no opportunity to give in a more extended or more homogeneous a context. The experimental methods used in the various measurements present little if any novelty, but are straightforward applications of methods previously used and published. No attempt will be made to give a final discussion or summing up, but any pertinent discussion will be given under the individual substances.

*Yttrium.* This material I owe to the courtesy of Dr. F. H. Spedding, Director of the Ames Laboratory of the Atomic Energy Commission. Although yttrium is not a member of the rare earth series of elements, it is very similar chemically and is naturally prepared by methods similar to those applicable to the rare earths. It became available for my measurements too late to be included in my paper on seven rare earth metals.[1] The material was supplied in a single massive hunk weighing 3 grams, from which pieces were cut with a cold chisel for the various measurements. The spectroscopic analysis made at the Ames Laboratory gave: Terbium, approximately 0.5 per cent; Dysprosium, approximately 0.2 per cent; Erbium, approximately 0.1 per cent; Holmium, not detected; Aluminum, Calcium, Magnesium and Silicon, weak; Iron, trace.

The density at room temperature and atmospheric pressure of the entire 3 gram piece, determined by weighing in air and in $CCl_4$, was 4.55. This is to be compared with 4.56 for similar material, determined at the Ames Laboratory by a pycnometer method. Widely divergent values in the literature are to be ascribed to chemical impurity and imperfect mechanical homogeneity.

The material is mechanically hard—so hard that no attempt was made to form it into wire by extrusion at elevated temperature, a method which had been successfully used for some of the rare earth metals. The specimens for resistance measurements to 30,000 were prepared from a chip by squeezing at 450° in an atmosphere of helium between carboloy platens covered with a thin layer of mica to prevent sticking, annealing to a bright red in a stream of helium, and filing to final thickness. This method of preparation

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demands the use of the "four razor blade" technique,[2] a method which gives only rough values for specific resistance, but good values for temperature and pressure coefficients, which do not demand precise control of the dimensions. The resistance to 100,000 was measured on a flake resulting from the shearing measurements to 100,000, which again was annealed to a red heat in helium after shearing. The correction required to bring the results to 100,000 into agreement with those to 30,000 was only 4 per cent, which is smaller than usual and presumptive evidence of the reliability of the measurements.

The specific resistance at atmospheric pressure at 0°C was $80 \times 10^{-6}$, which is in the middle of the range for the rare earth metals, excepting gadolinium and ytterbium. The temperature coefficient of resistance between 0°C and room temperature was 0.00271. This is lower than the value to be expected for a pure metal, but in line with the values for the rare earth metals. It would seem probable that the temperature coefficients of these metals are significantly less than 1/Abs. Temp.

The relative resistance at 24° as a function of pressure is given in Table I. Resistance decreases smoothly with increasing pressure

TABLE I

RESISTANCE OF YTTRIUM

| Pressure kg/cm² | $R_p/R_o$ |
|---|---|
| 1 | 1.0000 |
| 5,000 | .9900 |
| 10,000 | .9809 |
| 15,000 | .9724 |
| 20,000 | .9646 |
| 25,000 | .9568 |
| 30,000 | .9495 |
| 40,000 | .936 |
| 50,000 | .927 |
| 60,000 | .917 |
| 70,000 | .910 |
| 80,000 | .905 |
| 90,000 | .901 |
| 100,000 | .897 |

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with normal upward curvature with no evidence of abnormality of any sort. The magnitude of the pressure effect is one of the smallest for this series of metals, coming closest to that of praseodymium, which, however, exhibits anomalies.

*Compression.* Compression was measured to 40,000 in the conventional way. The yttrium was in the form of a short cylindrical slug, which was enclosed in a sheath of indium to transmit pressure hydrostatically. The results are given in Table II. Volume is a

TABLE II

COMPRESSION OF YTTRIUM

| Pressure kg/cm² | $\Delta V/V_0$ |
|---|---|
| 1 | .0000 |
| 5,000 | .0140 |
| 10,000 | .0265 |
| 15,000 | .0376 |
| 20,000 | .0474 |
| 25,000 | .0572 |
| 30,000 | .0670 |
| 35,000 | .0761 |
| 40,000 | .0852 |

smooth function of pressure. The numerical magnitude of the compression is in the neighborhood of the average of the rare earth metals. Its nearest neighbors are dysprosium and neodymium. The relative compressions at 40,000 of dysprosium, yttrium and neodymium are respectively: .0814, .0852, and .0955.

*Shearing.* The shearing strength was measured to 100,000 in the carboloy apparatus. For the first 50,000, shearing strength is concave toward the pressure axis, as is normal, but between 50,000 and 100,000 the curve becomes concave upward, an effect of which there are a number of other examples. The shearing strength at 50,000 is 2,700 kg/cm² and at 100,000 5,900. Lutecium, among the rare earth metals, shows a very similar curve.

*Rhenium.* Only recently has rhenium become available in massive form. It had formerly been available only as a finely divided powder. I had made shearing measurements on this powdered material and also measurements of the electrical resistance to 100,000

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on a coherent flake resulting from the shearing process.[3] The principal result of those measurements was that there is no evidence of any polymorphic transition up to 100,000. For the change of resistance a surprisingly large decrease was found for a material of so high a melting point.

The present results were obtained on a massive cast bar which I owe to the courtesy of the Kennecott Copper Corporation.

*Electrical Resistance.* This material is exceedingly hard and with my facilities could not be either rolled or swaged. For the resistance measurements thin slivers were worked out of the massive bar by grinding. This necessitated use of the "four razor blade" technique for the measurements to 30,000, so that the absolute value of specific resistance is of inferior accuracy. The temperature and pressure coefficients, however, should not be affected. Resistance as a function of pressure is given in Table III. Up to 30,000

TABLE III

RESISTANCE OF RHENIUM

| Pressure kg/cm² | $R_p/R_o$ |
|---|---|
| 1 | 1.000 |
| 10,000 | $.985_5$ |
| 20,000 | .971 |
| 30,000 | $.956_5$ |
| 40,000 | .944 |
| 50,000 | .936 |
| 60,000 | .927 |
| 70,000 | .920 |
| 80,000 | .912 |
| 90,000 | .906 |
| 100,000 | .901 |

there was no appreciable deviation from linearity: above 30,000 deviations from linearity in the normal direction (upward concavity) became appreciable. A negative correction of 30 per cent had to be applied to the decrements of resistance in the 100,000 apparatus to secure agreement with the results with the 30,000 apparatus; the sign of the correction is unusual.

The change of resistance under 100,000 now found for this massive material is 10 per cent, against 30 per cent formerly found

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for the material compacted by cold shearing from the powder. This only emphasizes the great difficulty which I have found many times of producing material of theoretical density from powders by the action of the highest feasible pressures in the cold. The difficulty would be expected to be particularly great for substances with great mechanical hardness and high melting point, of which rhenium is perhaps a unique example.

The specific resistance of this material at atmospheric pressure at 0°C was $10.6 \times 10^{-6}$, and the temperature coefficient between 0° and room temperature 0.00412. The high value of the latter gives presumptive evidence of high purity.

The change of resistance under 100,000 kg/cm² is very nearly the same as that of tungsten.

*Compression.* The dimensions of the massive specimen, which was in the form of a bar 2 cm long and 1.7 mm in diameter, were sufficient to permit accurate determinations of compression in the improved lever piezometer.[4] The compressibility is small, as is to be expected. Within error the relation between volume decrement and pressure is linear up to 30,000, the total change of volume at 30,000 being 0.00793. This gives for the average compressibility to 30,000:

$$\frac{1}{v_0}\left(\frac{\partial v}{\partial p}\right)_T = 2.64 \times 10^{-7},$$

pressure being measured in kg/cm².

Rhenium thus appears as the least compressible known metal. This position was hitherto held by iridium, the volume compression of which at 30,000 is 0.00818,[5] against 0.00793 above. The compression of tungsten is 0.00959 (single crystal). Diamond, however, remains the most incompressible substance, the volume decrement under 30,000 being only 0.0054, assuming linear compression.

Rhenium is too hard mechanically to permit the determination of its shearing strength with the present carboloy apparatus.

*Technetium.* The results on this are crude and only of orienting value. Professor Bainbridge had been making measurements of the effect of 100,000 kg/cm² on the rate of radioactive decay, and in the interpretation of the results it was important to know whether there was any polymorphic transition in the pressure range. Presumptive evidence could be obtained from measurements of resistance or of shearing to 100,000. If discontinuities or other

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abnormalities were shown by these measurements the presumption was good that there is a transition. On the other hand, it cannot be inferred from the absence of irregularities that there is no transition, since there are examples of known transitions not manifested in either resistance or shearing.

The material was prepared at the Brook Haven Laboratory, in the form of a powder, perfectly white and clean in appearance, unlike the rhenium powder formerly provided by them, which was black. The total amount of technetium was 0.20 gm. It was precompressed here into two discs 0.45 cm in diameter for the shearing measurements. In the shearing apparatus a smooth curve was obtained up to about 60,000 kg/cm$^2$. Here the shearing strength of the technetium became so great as to destroy the surface coherence of the carboloy blocks, so that no measurements could be made beyond this point. Pressure was pushed to 100,000 and the blocks rotated, at the expense of the carboloy surfaces, in order to compact the material as much as possible.

The conclusion from the shearing measurements is merely that they give no evidence of a transition up to 60,000.

The residue from the shearing experiments was in the form of thin coherent flakes from which it was possible to work out two specimens for resistance measurements to 100,000. The agreement between the runs on these two specimens was not good. Both showed initial irregularities, probably connected with further compaction of the material. Beyond 30,000 both gave a smooth decrease of resistance with pressure with normal upward curvature. The relative resistance at 50,000 and 100,000 of the specimen which exhibited the smaller decrease of resistance and for which the initial irregularities were less, and for which the compaction effects were therefore probably less, was respectively 0.835 and 0.773. The decrements are doubtless materially too large, as they were found to be for rhenium.

The resistance measurements on technetium give, therefore, no evidence of any transition above 30,000.

*Strontium.* The novel point of the measurements on this material was the extension of the temperature range to 200°C. Previous measurements have been made only at 30° and 75°[6] to 30,000 kg/cm$^2$; at the top of the pressure range a reversal of sign of the temperature coefficient was found, a highly unusual phenomenon.

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Since the apparatus was now available[7] for measuring resistance under pressure up to 200° it seemed of interest to examine strontium over the extended temperature range. The pressure range accessible at 200° was only 7,000 kg/cm², against the former 30,000.

The material for the present measurements was obtained from Professor King of Syracuse University in 1935, and has been kept sealed in glass in the dry state (not under oil). The seal has been broken several times during the intervening years to allow removal of small quantities for various purposes and immediately resealed. Measurements have not previously been made of its electrical resistance. For the present measurements it was extruded to wire 0.020 inch in diameter at a temperature of 230°. Four terminals were attached by spring clips and electrical resistance measured as a function of pressure by the regular potentiometer method at 0°, 100° and 200°C to 7,000 kg/cm². Pressure was transmitted by nitrogen. At 200° there were irregularities at a few points due to contact troubles, but not sufficient to obscure the results. At all temperatures, resistance is slightly concave upward as a function of pressure, as had been found previously. The curves of resistance at the three temperatures are parallel to each other within the limits

TABLE IV

RELATIVE RESISTANCE OF STRONTIUM

| Pressure kg/cm² | $R/R_0$ | | |
|---|---|---|---|
| | 0° | 100° | 200° |
| 0 | 1.000 | 1.283 | 1.762 |
| 3,500 | 1.186 | 1.486 | 1.970 |
| 7,000 | 1.435 | 1.725 | 2.199 |

of error. This means that the absolute increment of resistance for a fixed increment of temperature is independent of the pressure. Or, expressed otherwise, the temperature coefficient of resistance at any fixed temperature decreases with rising pressure inversely as the absolute resistance. These results therefore are inconsistent with a reversal of sign of temperature coefficient.

Resistance as a function of pressure and temperature is shown in Table IV. Note the rapidly increasing temperature coefficient with temperature at atmospheric pressure. The mean coefficient between

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0° and 100° is 0.00283. This material is therefore probably somewhat purer than the material formerly measured to 30,000 at 30° and 75°, for which the coefficient was 0.00240. It is however definitely less pure than some early material[8] on which I made measurements to 12,000, which had a temperature coefficient of 0.00383. At 0° the increase of resistance under pressure is closely the same as found on the former specimen measured to 12,000, but definitely greater than that of the specimen formerly measured to 30,000. It is therefore not unlikely that the reversal of temperature coefficient exhibited at the top pressure by the latter is in some way associated with impurity.

*Chromium.* Mr. H. L. Gilbert, Assistant Chief of the Bureau of Mines of the U. S. Department of the Interior at Albany, Oregon, was struck by the similarity of appearance between their tensile specimens of chromium fractured in tension at atmospheric pressure at 500°C, and some of my tensile specimens of tungsten, molybdenum and tantalum which had been fractured at room temperature at pressures high enough to greatly increase the ductility.[9] Mr. Gilbert suggested that it would be of interest to conduct tension tests on chromium at room temperature under hydrostatic pressure, and was so kind as to provide the material for the tests. This was in the form of rods four or five inches long ground to 3/16 inch diameter. The rods were "in the 'as-worked' condition having been finished at about 700°C." At room temperature the tensile fracture of these rods is completely brittle in character and the tensile strength only 12,000 psi. Drawn wires of the same material, from which the surface has been removed, give a tensile strength of 127,000 psi.

It was verified that this material is completely brittle at atmospheric pressure and room temperature. It was natural, therefore, to use the method devised for brittle material[10] in which the specimen is in the form of a simple cylinder, placed in simple mechanical juxtaposition to two steel pull pieces at the two ends, with a thin sheath of lead or copper over specimen and pull pieces to prevent access of pressure transmitting liquid to the surface between specimen and pull piece. The maximum tension that can be applied to the specimen in this method is numerically equal to the hydrostatic pressure, unless the specimen is artificially provided with a neck. This was not necessary in the present work.

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Three specimens were pulled to fracture under pressure. Several applications of pressure to the first specimen were necessary because of various mishaps to the apparatus. It was finally broken at an ambient pressure of 29,000 kg/cm$^2$. At this pressure the ductility was apparently complete, the specimen being necked down to a point too fine to measure. The second specimen was pulled to fracture in one stage at an ambient pressure at the moment of fracture of 13,300 kg/cm$^2$. The ratio of initial area to neck area at fracture

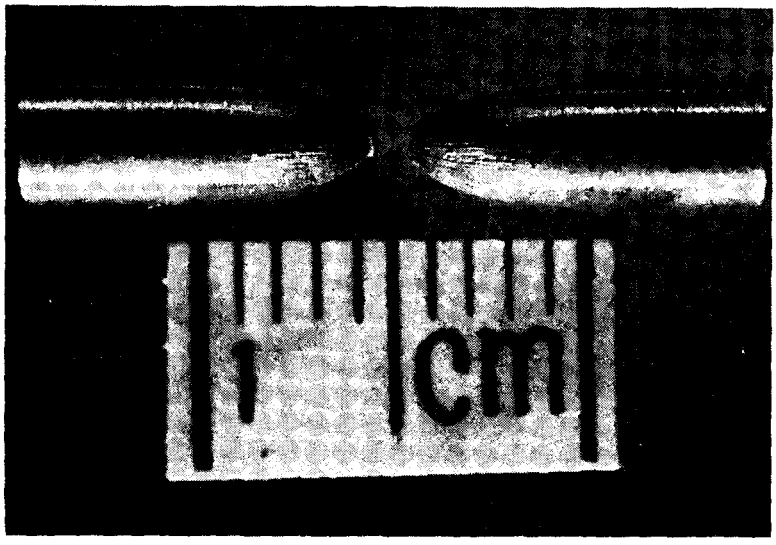


Figure 1. Tensile specimen of chromium, fractured at room temperature under an ambient pressure of 13,000 kg/cm$^2$.

was 25, corresponding to a reduction of area of 96 per cent, or natural strain ($\log_e A_o/A_f$) of 3.22. A photograph of this specimen is shown in Figure 1.

The third specimen was pulled to fracture in one stage at an ambient pressure at the moment of fracture of 9,900 kg/cm$^2$. The ratio of initial area to neck area at fracture was 14.05, corresponding to a reduction of area of 92.9 per cent, or a natural strain of 2.65.

Measurements were not made of the strain hardening as a function of extension and pressure; this would have demanded more extensive measurements in which the pulling was stopped at successive stages short of fracture. However, the measurements did

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give the maximum tensile load, from which the maximum load on the initial unstrained cross section can be calculated. This was approximately 8,800 kg/cm² for the specimen fractured under 29,000 kg/cm², 7,400 for the specimen fractured at 13,300, and 7,300 for the specimen fractured at 9,900. Pure chromium thus appears as one of the softer metals. The effect of pressure in increasing ductility is in the expected direction. The extreme brittleness at atmospheric pressure appears, however, to be somewhat of a puzzle.

*Germanium.* Under normal conditions germanium is excessively brittle. Since it crystallizes in the diamond lattice particular interest attaches to finding whether ductility is imparted by hydrostatic pressure. No previous investigations have been made of the effect of pressure on the tensile properties of any other substance crystallizing in this system.

Unusual experimental difficulties were encountered, the apparatus exhibiting a long run of obscure leaks, the probable reason for which being finally traced to slight changes in the composition of the packing. Data sufficient to throw light on the point at issue were obtained on three specimens of germanium from two different sources. The first material was from the Bell Telephone Laboratories, " n-type, As doped 100 seed, specific resistance = 6.6 ohm cm," in the form of a single crystal rod. It was turned to final dimensions with a carboloy tool. The specimens were in the form of simple cylinders, mounted with sheath and steel pull pieces like the chromium described in the previous section. With the first specimen the maximum safe load was reached without fracture. The ambient pressure was 26,000 kg/cm², and the maximum load was 18,800 kg/cm² on the original section. The second specimen of the same material was made of smaller diameter, so that the same total load would give a greater intensity of stress. With this specimen, at an ambient pressure of about 25,000 kg/cm², fracture occurred at about 25,000 kg/cm² on the original section. This fracture was due to the separation of the copper sheath, which occurs when the tensile pull reaches its maximum possible value, namely the ambient pressure. The specimen itself showed no sign whatever of necking or permanent alteration of dimensions. It was separated into two pieces along a perfectly clean cut plane perpendicular to the axis, a fracture often found in rods of glass pulled under

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similar conditions. It is evidence of some internal atomic rearrangement, too slight to be disclosed by large scale measurements.

The third specimen was cut from a rod obtained from the Raytheon Company. Beyond the fact that it was of high purity and was in single crystal form its specifications are not known. This specimen was turned with a neck of such dimensions that the limiting tensile stress was twice the hydrostatic pressure. It was mounted in a combination copper and lead sheath, the lead being so disposed as to permit folding down around the neck. With this specimen an ambient pressure of 27,000 kg/cm$^2$ was reached, at which there was slight leak, sufficient to result in the fracture of the specimen under such conditions that no measurements could be made of the load. The fracture was at the neck, not by pulling apart at the ends. The only numerical conclusion that can be drawn from this is that the tensile breaking strength under 27,000 kg/cm$^2$ pressure is less than 54,000 kg/cm$^2$. We already know from the previous experiment that the tensile strength under 25,000 is greater than 25,000 kg/cm$^2$.

The character of the fracture of the third specimen was conchoidal, glass-like, with no evidence of crystalline or other slip.

The general conclusion is, therefore, that a pressure of 27,000 kg/cm$^2$ produces no measurable ductility in germanium, and that its tensile strength under these conditions is of the order of at least 30,000 kg/cm$^2$. It is natural to associate these properties with the crystal system.

*Glass.* It has already been found[11] that glass may exhibit permanent changes of density after exposure to high hydrostatic pressure in conjunction with some shearing stress. Since it is known that this shearing stress produces permanent alterations of shape, that is, that permanent flow is produced by the shearing stress, it is natural to ask whether a permanent increase of density would be produced by pure hydrostatic pressure, without the cooperation of flow. A very natural picture of the nature of the process as consisting of the molecules finding new resting places as they slide over each other would suggest that it would not.

The technique which I have employed[12] in measuring resistance to 100,000 kg/cm$^2$ makes it possible to apply very approximately hydrostatic pressure to small pieces of glass.

For this purpose the thickness of the pipestone cell in which the

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pressure is confined was increased from 0.010 to 0.015 inch, the transmitting medium was changed from silver chloride to lead, and the width of the retaining pipestone cell increased from 0.047 to 0.062 inch. The material experimented on was soda glass, in the form of a disc 0.006 inch thick and 0.125 inch in diameter. It was enclosed in lead in the center of the pipestone cell and pressure to 100,000 applied between carboloy platens in the regular way. Two applications of 100,000 to two different specimens produced no change of thickness of as much as 0.0001 inch. The glass was cracked into several clear blocks by the treatment.

Previously,[11] increases of density of several per cent have been found after exposure to pressures of this magnitude combined with shearing stress and deformation. We may conclude that the plastic shearing deformation plays an essential role in the increase of density.

*Fluorothene.* This is a fluorinated compound of the composition

$$\left| \begin{matrix} F & F \\ | & | \\ -C & -C- \\ | & | \\ Cl & Cl \end{matrix} \right|_n.$$

I owe a sample to the courtesy of the Bakelite Company. In the following (Table V) values are given for the compression to 40,000 kg/cm². This was determined in my regular apparatus for this pressure range.

TABLE V

COMPRESSION OF FLUOROTHENE

| Pressure kg/cm² | $\Delta V/V_0$ |
|---|---|
| 1 | .0000 |
| 3,540 | .0453 |
| | .0534 |
| 5,000 | .0682 |
| 10,000 | .1045 |
| 15,000 | .1319 |
| 20,000 | .1521 |
| 25,000 | .1686 |
| 30,000 | .1824 |
| 35,000 | .1935 |
| 40,000 | .2022 |

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The particular point of interest in making these measurements was to find whether this material exhibits a quasi-polymorphic transition under pressure in the same way that "teflon" does.[13] A volume discontinuity was indeed found for fluorothene, but at a lower pressure and somewhat less in amount than for teflon.

The occurrence of volume discontinuities in material of this constitution is somewhat unexpected, and must indicate an approach to at least some aspects of a crystalline arrangement.

*Lead.* It was recently called to my attention by Mr. S. J. Jacobs of the U. S. Naval Ordnance Laboratory that I had published no values for the compression of lead, although I had referred in print in 1946[14] to unpublished data for the compressions of copper, aluminum, and lead. Compressions of copper and aluminum to 30,000 by the improved lever piezometer were subsequently published,[4] but by inadvertence the values for lead were never published. These are now given in Table VI copied directly from my

TABLE VI

COMPRESSION OF LEAD

| Pressure kg/cm² | $\Delta V/V_0$ 23° | 75° |
|---|---|---|
| 5,000 | .01118 | .01150 |
| 10,000 | .02186 | .02238 |
| 15,000 | .03213 | .03273 |
| 20,000 | .04192 | .04262 |
| 25,000 | .05125 | .05210 |
| 30,000 | .06005 | .06212 |

note book of 1939. The measurements were made with an older form of lever piezometer. However, the absolute compressibility of lead is so high that the accuracy should be as good as that for less compressible metals in the improved apparatus. The lead was of 99.9999 purity, the same material as used in many of my other measurements.

*Compression of Hen's Egg Yolk and White.* The following measurements were made in 1948 at the request of Professor Douglas Marsland of New York University, who said that they would be of some biological interest and that apparently no such measurements were in the literature.

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The possible pressure range of such a measurement is not much more than 5,000 kg/cm$^2$ because of the onset of coagulation at higher pressures. The measurements were accordingly made with a recent form of apparatus[15] which permits rapid determinations of the compression of liquids to 5,000 kg/cm$^2$ by a modified free piston technique. The material was two fresh unfertilized hen's eggs obtained from a local dealer. The whites were separated from the yolks by my wife by a well known feminine technique. The whites were homogenized by stirring and rubbing with the finger. Both whites and yolks were exhausted to a moderate vacuum to remove the bulk of the air without removing an appreciable amount of water.

## TABLE VII

COMPRESSION OF WATER, HEN'S EGG YOLK AND HEN'S EGG WHITE AT 22.5°C.

| Pressure kg/cm$^2$ | $-\Delta V/V_0$ | | |
|---|---|---|---|
| | Water | Yolk | White |
| 500 | .0210 | .0203 | .0184 |
| 1,000 | .0387 | .0371 | .0347 |
| 1,500 | .0544 | .0519 | .0493 |
| 2,000 | .0686 | .0650 | .0623 |
| 2,500 | .0814 | .0769 | .0742 |
| 3,000 | .0930 | .0877 | .0851 |
| 3,500 | .1036 | .0975 | .0951 |
| 4,000 | .1132 | .1063 | .1044 |
| 4,500 | .1222 | .1143 | .1130 |
| 5,000 | .1308 | .1215 | .1210 |

The results are shown in Table VII. Water is included in the same table, since the chief interest in the results was the comparison with water. It is not to be assumed that the values thus given for water are the absolutely best values which are to replace values previously obtained with other and better apparatus. It is merely that the values here given for water were determined in the same apparatus and at the same time as those for the egg material, and thus offer the best comparison.

It will be seen from the table that both white and yolk are some-

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what less compressible than pure water, that up to 2,500 kg/cm$^2$ the white is less compressible than the yolk, and above 2,500 more compressible.

A slight degree of coagulation was produced by 5,000, but not enough to affect the compressibility, the measurements with decreasing pressure being indistinguishable from those with increasing pressure. The yolk was stiffened so much that it would not pour out of the pressure vessel on inverting; the coagulation of the white was less, inasmuch as it did pour.

*Electrical Resistance during Plastic Extension under Pressure.* It is not uncommon to compare the resistance of a wire in the virgin condition and after it has been permanently stretched; there are a few measurements of the changing resistance of a wire during the process of plastic extension at atmospheric pressure, but as far as I know the change of resistance has never been studied during the process of plastic extension in a medium under hydrostatic pressure. This might be expected to be of some interest because the voids formed in the metal by the process of plastic extension should be materially altered by pressure.

An apparatus was constructed for this sort of measurement and a few measurements made on copper and iron. Tension is applied to the wire by a simple modification of the apparatus used in studying the tensile properties of metals under pressure.[16] Measurements of resistance are made with a potentiometer technique, using four terminals attached to the specimen. The length of the tension specimens was of the order of 3.5 cm and the diameter 1.7 mm. The diameter had to be made small to bring the resistance to a high enough value to be within the sensitiveness of the electrical measurements. A small diameter means a comparatively small tensile load and therefore high sensitivity in the load measuring device. This was a "grid" of the same general construction as the grid formerly used, but made as thin as possible to give sensitivity. This means a grid of high fragility, difficult to handle. It was fracture of the grid that finally terminated these measurements, which were not resumed because other more important work was waiting.

The method demands the use of seven electrically insulated leads into the pressure chamber: three to measure the resistance of the specimen, three to measure the resistance of the grid which gives the tensile load, and one to measure the pressure with the manganin

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gauge. A common ground, the apparatus itself, is used for all three measurements. The seven terminal plug is the same as that used previously[17] in measurements of compression to 100,000 kg/cm$^2$. As in the previous measurements the apparatus is so arranged that during the first part of the stroke of the piston only hydrostatic pressure is built up. When a prearranged pressure is reached, which can be controlled by varying the amount of liquid in the apparatus or by the use of suitable stops, the piston makes contact with the tension member. Further advance of the piston stretches the tension member as well as increasing the pressure. By suitably varying the pressure at which contact is made, the change of resistance during the stretching process may be studied at different mean pressures.

The only measurement of the length of the specimen during tension was afforded by measurements of the position of the piston. This includes the contribution of the distortions in various parts of the apparatus; these were large enough to mask the changes of length of the wire itself during the elastic part of the range. During the plastic part of the extension, when the displacements are much larger, the piston displacements give a rather good picture of the elongation of the specimen itself.

Measurements were made at room temperature on commercial copper and Armco iron. In addition to control measurements at atmospheric pressure, two specimens of copper were measured, one at a mean pressure of 4,500 kg/cm$^2$ and the other at a mean pressure of 17,000 kg/cm$^2$, and one specimen of iron at a mean pressure of 22,000 kg/cm$^2$. Plastic extension was purposely kept in the initial range, reaching the necking point as nearly as possible. Perceptible necking had not started in the copper specimens — in the iron it was just perceptible.

Several ranges are to be distinguished. In the first place there is the range of pure hydrostatic pressure; here the question of interest is the comparison of the pressure coefficient of the wire in the virgin condition and after it has been plastically stretched. In the range during which tensile load is acting there is to be considered the effect of stretching on resistance during the initial elastic part of the cycle, then the effect of stretch on resistance during plastic extension, and finally the change of resistance during tensile unloading after maximum plastic stretch. In general, these three effects are functions of mean pressure.

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For both copper and iron the resistance decreases under hydrostatic pressure and increases with increase of length under tension. The following results were obtained:

*For copper.* The pure pressure coefficient of resistance of the specimen pulled at a mean pressure of 4,500 kg/cm$^2$ was 33 per cent less numerically immediately after it had been elongated permanently up to approximately the necking point than it was in the virgin condition. The specimen pulled at a mean pressure of 17,000 kg/cm$^2$, on the other hand, showed no certain difference of pressure coefficient between the permanently elongated and virgin condition.

There is an abrupt increase of the slope of the curve of resistance versus length on passing from the elastic region to the region of permanent set. At atmospheric pressure the ratio of the two slopes may be as great as 7. When pulling under pressure, the ratio of the two slopes becomes less, dropping to something of the order of 2. There was no certain effect of pressure on this ratio. This is as one would expect, the cavities opened up in the structure during plastic flow being less important when the flow occurs under pressure, because the pressure pushes the cavities together again.

During release of tensile load after pulling to maximum elongation, there were prominent non-linear effects in the relation between resistance and load. The data were not sufficient to establish the nature of the effect of pressure on the relative tension coefficients of virgin and permanently stretched material.

*For Armco Iron.* The pure pressure coefficient of resistance of iron in the virgin condition and permanently stretched to the necking point under a mean pressure of 22,000 kg/cm$^2$ was practically the same.

At atmospheric pressure the slope of the curve of resistance versus length increases by a factor of 2.7 on passing from the elastic to the plastic range. At 18,000 kg/cm$^2$, the pressure at which plastic extension first occurred, the slope increases by a factor of 3.8 on passing from the elastic to the plastic range. This direction of change is the opposite of that found in copper, and not expected.

At 27,000 kg/cm$^2$, the pressure of maximum extension and the pressure at which release of the tensile load began, the slope of the curve of resistance against length on the beginning of release of tensile load is 5.3 times greater than on the virgin specimen. This

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again is not in the expected direction. It is to be remarked, however, that there are marked deviations from linearity during release of tensile load after stretching to the necking point.

It is to be regretted that fracture of the grid terminated these measurements. The difference of the effect in iron and copper suggests that there is material here for further investigation.

I am indebted to Mr. L. H. Abbot and Mr. Charles E. Chase for assistance with many of the experiments of this paper.

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